Heavy Metals in the Overlying Water and Bottom Sediments of Shing Mun River and Inner Tolo Harbour

by

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ABSTRACT

This study aims at studying the concentration and speciation of heavy metals in the water and bottom sediments of a tidal channel and its estuaries, remobilization of metals from the sediments and the role of acid volatile sulfide (AVS) in metal toxicity mediation. This investigation is useful in revealing the movement, fate and potential risks of heavy metals to the biota and mankind.

The results of this study suggest that both the water and the sediments in the study area contain elevated levels of heavy metals discharged from the electronic and electroplating industries in the river catchment area. In spite of the high metal contents in the water column, only 10-30% of the metals exist in the labile form. As metals occurring in the labile form are in the ppb range, the risks posed to the aquatic organisms are probably small.

Elevated metal level in the water column are also reflected in high metal content in bottom sediments. However, only about one-third of the metals in bottom sediments occurs in the stable residual crystalline forms. The majority are either associated with sulfides, organic matters, and Fe-Mn oxides.

Substantial amount of AVS in the bottom sediments provides sufficient buffer to react with metals to render them less bioavailable to the biota. Although some labile metals still exist in the pore water, the occurrence of labile metals only account for 0.1-0.4% of the total metals present in the water-sediment matrix.

Labile metal contents in pore water is also much less than that in the overlying water. All these evidences point to the important role of AVS in metal toxicity mediation.

As mentioned above, metals are mainly bound to AVS, organic matter or Fe-Mn oxides. These metal-binding phases are subjected to external environmental changes. However, the seasonal variation of the physiochemical water properties are not adequate to effect any significant remobilization of metals. The reducing condition of the bottom sediments provides a stable environment for the formation of AVS and can prevent the loss of AVS due to oxidation. This helps to reduce the metal bioavailability.

As a result, the risk posed by the metals to marine organisms may not be as great as what the total metal concentration figures may suggest. However, this does not mean the bottom sediment would never pose any problem to the environment. In fact, the disturbances of bottom sediment and their subsequential disposal will change the ambient water quality which may facilitate the remobilization of metals.

Most importantly, this study throws light on the necessity of re-examining the existing sediment quality criteria based merely on the total metal content. Measurement of the total metal concentration is, obviously, not a reliable indication of the potential metal toxicity. More attention should be focused on the chemical speciation, and other co-existing substance, such as AVS, that may mediate metal toxicity.

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CHAPTER 1

INTRODUCTION

Heavy metal toxicity is one of the most significant forms of pollution in the environment. In an aquatic system, metals are present in both the water column and the bottom sediment pool. The exchange of metals between the two depends on the chemical and physical processes at the sediment-water interface. The water column is traditionally regarded as a receiving body for effluents with lots of metallic toxicants. Heavy metals introduced into the aquatic environment may partition among various compartments through different processes such as sorption, desorption, precipitation, solubilization, coagulation, flocculation and complexation (Forstner and Witmann, 1979). Finally, they will settle out of the water column and deposit onto the sea bottom to become part of the sediment pool. Since most metals are being held up in the sediment pool in the aquatic system, study of the occurrence of heavy metals and their interactions with co-occurring substances in the sediments will give a better understanding of the sources, sinks and pathways of metal pollution. On the other hand, since metals in different sediment partitioning phases may exhibit different toxicity levels, measurement of the concentration of metals will not provide an estimation of the harmful impacts of metals on the aquatic environment. In view of this, a proper assessment of the pollution risk is called for to ascertain the percentage of metals that are bioavailable.

Heavy metals immobilized in bottom sediments do not remain unchanged. With the continuous influx of metals and changing of water properties, the equilibrium at the interface between sediment and water can be upset, thus initiating the immobilization or remobilization processes. Consequently, metals are locked up or released in response to changes in the aquatic environment (Lu and Chen, 1977).

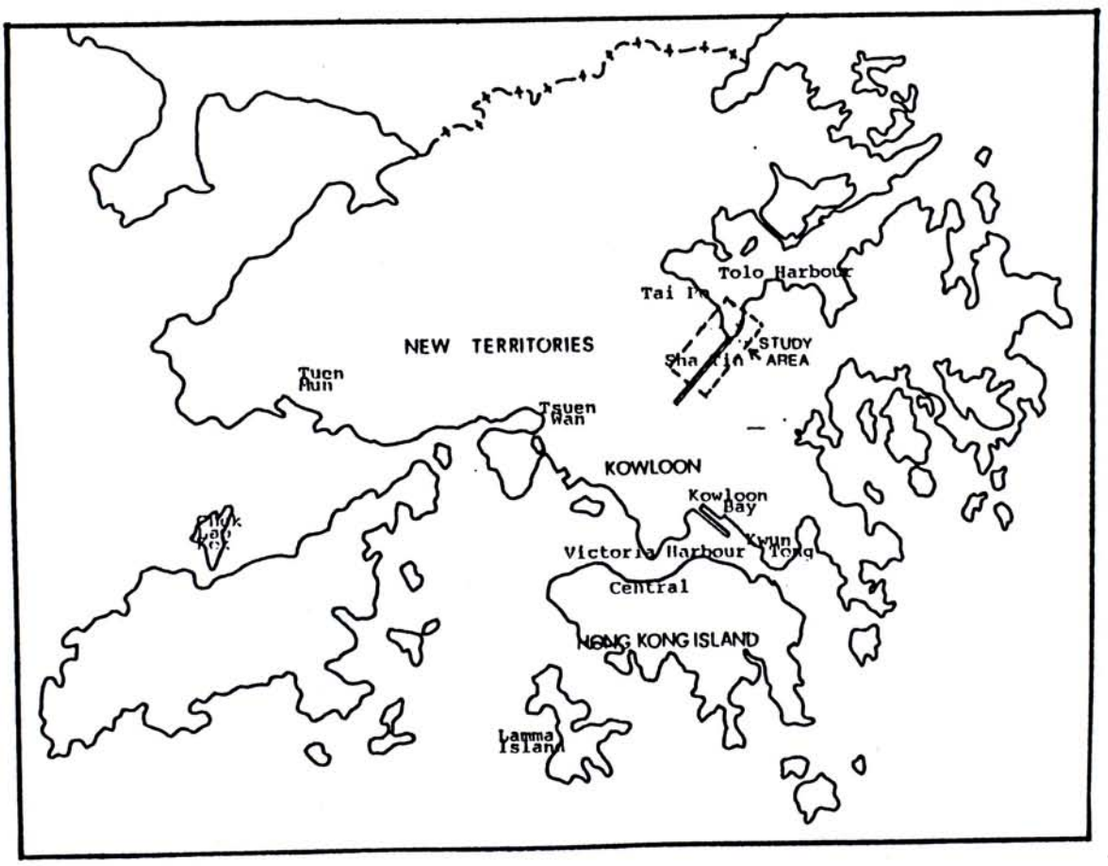
The easiness of metals to be remobilized depends greatly on the chemical form in which they exist. Since the various partitioning phases have a significant bearing on the metal bioavailability, this study is going to examine the distribution of various metal speciations in a channel-estuary setting with rapid fluctuations in physicochemical properties of the overlying water.

In anoxic sediments, such as those found in most coastal areas in Hong Kong, the existence of sulfur and sulfide is probably the dominant factor in determining the bioavailability of heavy metals. A number of previous studies have documented that sulfides, especially acid volatile sulfide (AVS), can scavenge metals in the sediments (Di Toro et al., 1990). This study, therefore, is going to unravel the relationship between AVS and metal bioavailability in an aquatic system. Since the concentration of AVS in sediments is known to vary over space and time, it is important to ascertain the spatial and temporal variation of AVS in the study area before the assessment of AVS in mediating metals begins.

The study of metal pollution is important in Hong Kong because there are numerous factories discharging a wide variety of industrial wastes, sewage and

industrial effluents into the sea from the urban centers embracing the Victoria Harbour and situated on the coast at Tai Po, Shatin and Tuen Mun (Figure 1.1) (Moore and Harriss, 1974; Yim and Fung, 1981). The Environmental Protection Department (EPD) reported in 1994 that the bottom sediments near the urbanized centers, such as Victoria Harbour, Tsuen Wan and Kowloon Bay, contained extremely high concentrations of chromium (greater than 70 μg/g dry solids), zinc (greater than 140 μg/g dry solids) and copper (greater than 400 μg/g dry solids). The heavy metal concentrations in the sediments of inner Tolo Harbour, Deep Bay and the north western waters were also high (EPD, 1994a).

Figure 1.1. Location of the Study Area



In the light of the above background, this study attempts to:

1. evaluate the occurrence and speciation of metals in the sediments and the water column of a tidal inlet in Hong Kong;
2. examine the spatial and temporal variation of AVS;
3. assess the role of AVS in mediating metal toxicity; and
4. assess the overall metal bioavailability level.

The rest of this chapter will review previous studies on heavy metal pollution in Hong Kong, the speciation of metals in waters and sediments, as well as the role of AVS in metal contaminated sediments.

1.1 PREVIOUS HEAVY METAL STUDIES OF HONG KONG MARINE WATERS AND SEDIMENTS

In Hong Kong, millions of gallons of untreated sewage containing toxic heavy metals are discharged into the sea everyday. These heavy metals have adverse effects on the biota and, in some cases, on human beings. As a result, many researchers have assessed the occurrence of metals in the aquatic environment. The first report on heavy metals in the Hong Kong marine waters (Chan et al., 1974) indicated an elevated level of metal concentration in the Victoria Harbour. Subsequent studies also confirmed the occurrence of metals, together with organochlorines and other pollutants (Morton, 1989; Phillips, 1989; Wu, 1988).

Given the difficulty in obtaining accurate measurement of long term concentration of heavy metals in the marine environment, aquatic organisms are used by some researchers to monitor the toxic effects of metals. It was found that elevated bioavailability of Cu, Fe, Mg and Zn were evident in North-East New Territories (Wong and Li, 1977; Wong et al., 1978; Wong et al., 1979) and the entire Victoria Harbour was heavily contaminated by Cu, Zn and Pb (Phillips, 1979; Phillips, 1984; Phillips and Yim, 1981).

Besides using marine organisms, some researchers focused on the metal contents in the sediment pool which served as an indicator of the metal pollution (Hong, 1992; Yim and Fung, 1981). During the process of sedimentation, metals in the water column may be adsorbed by the suspended sediments or organic matters that consequently settle to the sea bottom. As a result, the bottom sediments serve as an important sink for the pollutants. Yim and Fung (1981) were the first to study the geochemical composition of sediments in Hong Kong, and reported high levels of Cu, Pb, As, Zn and a moderate amount of Cr in the Victoria Harbour. Meanwhile, the Environmental Protection Department (EPD) has a continuous program to monitor the metal concentrations in the water and sediments at some 70 sampling locations in the Hong Kong territorial waters.

Most of the previous studies have a common limitation as they only focused on the concentration of the metals and leaving the various speciations in which the metals exist unattended. To rely merely on the concentration as an indicator of the

effects of these metallic toxicants is inadequate (Tessier and Campbell, 1987). It has been established in the last decade that the toxicity of metals in the sediments is closely related to the chemical forms that metals exist. Therefore, the study of speciation of metals in the aquatic environment is very important. At a given level of metal concentration, the difference in the physiochemical properties among sediment types may result in different amounts of heavy metals available to the biota (Di Toro et al., 1990).

For this reason, the attention of this study has been given to the assessment of bioavailability of metals in water and bottom sediments. Two recent marine sediment studies done by Hong (1992) and Kwok (1993) have also focused on different speciation of metals in the contaminated sediments of Victoria Harbour and Tsuen Wan, respectively. These studies provide a good background for this study.

1.2 METAL SPECIATIONS IN AQUATIC ENVIRONMENT

One of the turning points in the field of aquatic chemistry is the development of new concepts on metal speciations in the aquatic environment. Then, it becomes apparent that the knowledge of metal concentrations alone will not be sufficient to benefit the understanding of their behavior, their biogeochemical cycles, and their ecotoxicity in an aquatic environment. The study of metal speciations was defined by Florence (1982) as "the determination of the individual physiochemical forms of

the element which together make up its total concentration" (Salomons and Forstner, 1984). There are different fractionation schemes for metals in water and sediments.

1.2.1 Speciation of Metals in Water

There are various methods to determine the speciation of heavy metals in solution. The first and still the most comprehensive scheme was the one used by Batley and Florence (1976). The scheme divided the sample in fractions by passing in 0.45μm nominal pore size filter and separating the "particulate" metals from the "dissolved" metals. Size fractionation is a useful technique for speciation study since the bioavailable fraction is generally associated with the smaller size categories. The "dissolved" metal fraction is, then, measured with anodic stripping voltammetry (ASV) making a distinction possible between ASV-labile and non-ASV-labile fractions, or called bound fraction (Salomons and Forstner, 1984).

A number of studies have provided evidence that the free metal ions were accountable for the toxic metal species for organisms (Salomons and Forstner, 1984). Therefore, understanding the concentration of labile metals and the fraction in the total amount is crucial in the assessment of metal bioavailability.

1.2.2 Speciation of Metals in Bottom Sediments

Owing to the complexity of the physical and chemical processes that occur in nature, heavy metals are associated with bottom sediments occurring in a variety of

physiochemical forms, commonly known as partitions. The forms in which metals exist in oxic and anoxic sediments can be very different.

In oxic sediments (i.e., in an oxidation condition with Eh value larger than 0 mv), metal partitioning is very complex (Campbell et al., 1988; Oakley et al., 1981; Swartz et al., 1985; Swartz et al., 1990) and the most important partitioning fractions are:

1. adsorption on surfaces of amorphous or crystalline iron and manganese oxides, and clay minerals;
2. with organic matters;
3. in the lattices of secondary minerals, or occluded in amorphous compounds; and
4. in the lattices of undecomposed primary minerals.

On the other hand, metal partitioning in anoxic sediments (i.e. sediments in reducing condition with Eh value smaller than 0 mv) is less complex. Insoluble sulfides are believed to be the dominant metal binding phase since sulfur and sulfides are most abundant in anoxic sediments and pore water (Morel et al., 1973).

Therefore, the subsurface anoxic region is the main reservoir for metals within the sediment pool (Davies-Colley et al., 1985).

When Tessier and others (1979) studied the partitioning phase of heavy metals in the sediments, they summarized all the possible metal binding phases in both oxic and anoxic sediments and classified them into five phases: (1)

exchangeable, (2) bonded to carbonates, (3) bonded to Fe-Mn oxides, (4) bonded to organic matters and sulfide and (5) residual. With the exception of the residual fraction, metals that temporarily immobilized on the suspended matter and in bottom sediments of aquatic systems may be released under the alteration of aquatic environment such as lowering of the pH, increased salinity, changes in the redox conditions, and increased input of organic chelators (Salomons and Forstner, 1984). For this reason, study of metal speciations is useful in estimating the metal remobilization under changing environmental conditions and thus throws light on potential uptake of metals by biota.

Among different metal binding phases, sulfide, especially AVS, in the Hong Kong coastal marine sediments merits detailed investigation. In Hong Kong, most coastal sediments exists in a reducing environment is covered by a thin, oxidized surface layer of sediments. In these anoxic sediments, while adsorbing surfaces and organic carbon may affect the partitioning (Oakley et al., 1981), AVS should be the dominant phase in controlling metal bioavailability. Since AVS is the primary metal mediator in the anoxic sediments, it informs of the toxicity level of the environment and hence infers the level of metal bioavailability in the study area. The following section will briefly outline the formation of AVS and its mediation role in controlling metal bioavailability and hence toxicity in sediments.

In this study, therefore, bioavailability of metal is assessed by the lability of metals in water, probability of metal remobilization to the water column and toxicity

level in the sediments as indicated by simultaneously extracted metals (SEM)/AVS. (SEM is the metals extracted during AVS analysis)

1.3 AVS IN MARINE SEDIMENTS

1.3.1 Formation of AVS

In the biological respiratory process, heterotrophic organisms oxidize organic molecules to obtain energy. Since sulfate is the most abundant electron acceptor in seawater, it will be the primary oxidant for the organic carbon oxidation reaction once oxygen is exhausted (Lin, 1990).

In the sediment pool, sulfate reduction is also an important process particularly in an anoxic environment. It was reported that sulfate reduction could account for 53% of total mineralization of organic matters in the sediments (Jorgensen, 1977). During the reduction process, the sulfate and sulfur groups are reduced by dissimilatory sulfate reducing bacteria, such as *Desulfovibrio* and *Desulfotomaculum spp*, as part of their respiratory process (Pasgate, 1984). Hydrogen sulfide (H_2S) is ultimately excreted as the respiratory end-product.

Among the sulfide produced, 10% may end up forming metal sulfides (Jorgensen, 1977). Dissolved metal ions in the water can react with the hydrogen sulfide and other sulfur compounds. Since iron is the most abundant sulfide-forming

metal in sediments, metal sulfides are dominantly iron sulfides (Morse et al., 1987). The concentration of iron sulfide minerals in recent sediments is often categorized "operationally" into two classes. One is pyrite (FeS_2). The other is acid volatile sulfide (AVS), which is a solid-phase sulfide soluble in cold acid. This fraction includes mainly amorphous iron sulfide, mackinawite, and greigite. AVS is just a meta-stable sulfide species, but it may persist for a long time in the sediments due to its slow transformation rate (Berner, 1967; Goldhober and Kaplan, 1974). By forming the nonbioavailable and insoluble metal sulfides, AVS can control the metal bioavailability in the anoxic sediments (Boulegue, 1983; Davies-Colley et al., 1985; Krauskopf, 1956; Leckie and James, 1974; Lu and Chen, 1977).

AVS includes both dissolved sulfides and amorphous iron monosulfides. Since dissolved sulfides only exist in very small amounts, most previous studies of AVS concentrated only on the solid phase of AVS. As a result, the term acid-volatile sulfide (AVS) has been conventionally used to define the sulfide fraction removed from sediments by acid extraction, usually by HCl.

1.3.2 Seasonal and Spatial Variation of AVS

AVS in aquatic sediments is controlled by a number of physiochemical factors, namely, (1) existence of iron, (2) existence of sulfate, (3) reactivity of organic matters, (4) sediment grain size, (5) sedimentation rate and (6) overlying water temperature. As these controlling factors vary, the concentration of AVS varies in time and space in marine sediments.

A number of studies on AVS in freshwater lakes and marine coastal sediments (Howard and Evan, 1993; Jorgensen, 1977; Leonard et al., 1993) showed that anoxic conditions, depth of sampling site and AVS concentration are inter-related. It was also found that the seasonal variation of AVS concentrations in both marine and freshwater sediments followed a similar temporal trend. In summer, an optimum sulfate reduction rate occurs when water temperature is very high. Moreover, the oxygen consumption rate is greater because of microbial decomposition which results in an anoxic environment at the sediment-water interface. This anoxic environment favours the formation of AVS (Leonard et al., 1993). This explains why AVS concentration is higher in summer than in winter.

The concentrations of AVS also vary with sediment depth. The highest AVS concentration is always found at a depth of 5-10 cm beneath which, the FeS concentration decreases rapidly due to pyritization (Jorgensen, 1977). These variations with depth are related to the biotic factor. There is a large population of marine organisms at the top layer which can enhance the formation of AVS by increased incorportation of deposited organic matters into the sediments (Davies-Colley et al., 1985).

The studies described above indicate clearly that the formation of AVS varies remarkably with both depth and seasons. As a result, in the absence of alternative binding phases, metals may be reintroduced from the sediments to the overlying water and may become bioavailable during certain times of the year. To address this

problem, a study of the seasonal variation of AVS concentrations at different sediment depths is necessary. This study is to provide not only a better understanding of the variations in AVS levels but also the effect on sediment toxicity.

1.3.3 AVS as Mediator of Metal Toxicity

Although AVS has been the subject of investigation for many years, most of the earlier works focused on AVS in the sulfur cycle (Jorgensen, 1977; Morse et al., 1987). The significance of AVS in mediating metal toxicity has became apparent only after the study conducted by Di Toro and others (1990). The reason for the lack of attention before was due to the fact that sediments contain very little free sulfide. Even if there is a trace of free sulfide, it will be quickly degassed from the system under normal conditions to form H_2S.

Di Toro and others (1990) were the pioneers to highlight the significance of AVS in mediating metal bioavailability. They hypothesized that not only free sulfides, but also the sulfides in some amorphous metal sulfides, are available for binding with metals. It was found that when the molar ratio of metals to AVS exceeded 1 (i.e., the AVS binding pool was exhausted), interstitial water concentrations of free cadmium would increase dramatically and there would be a corresponding increase in the mortality of the tested organisms. Therefore, AVS was proposed as a parameter in normalizing metal availability in sediments and as part of the equilibrium partitioning approach to establish sediment quality criteria.

Di Toro and others (1990) also suggested that the lowest limit of AVS for sediment metal normalization was 1 μmol AVS/g of wet sediments. Below this value, other oxidized ligands, such as iron oxyhydroxides, will become much more significant than AVS.

Further experiments with Cd, Zn, Ni, and Cu, demonstrated that basing on the ratio of Simultaneously Extracted Metals (SEM) and AVS in the tested sediments, acute toxicity to organism could be predicted (Ankley et al., 1991; Carlson et al., 1991; Di Toro et al., 1992). All these works reach a similar conclusion that normalization of certain metals to AVS is a reliable tool for sediment toxicity assessments (Ankley et al., 1993; Ankley et al., 1994a; Casas and Crecelius, 1994; Di Toro et al., 1992; Pesch et al., 1995).

Even in the long-term studies conducted by Ankley and others (1994a), the metal concentration in the tested organisms held in the sediments was similar to the concentrations in worms held in clean water after thirty-day exposure. This indicates that it is feasible to use metal/AVS relationship to predict metal exposure in both long-term and short-term studies with benthic invertebrates.

In short, SEM/AVS ratio has been used to predict the bioavailability and hence the toxicity of metals to aquatic life (Ankley et al., 1991). When the SEM/AVS ratio is less than one, the sediments is not toxic. Therefore, AVS actually sets the boundary between low metal activity and high metal activity.

1.3.4 Chemical Basis for AVS Sediment Normalization

Water column experiments, both in the laboratory and *in situ*, have demonstrated that biological effects, induced by metal toxicity, correlate primarily to the divalent metal activity (Me^{2+}) (Ankley et al., 1991; Sunda et al., 1978; Sunda and Guillard, 1976). The chemical basis for the primacy of AVS in determining the toxicity of metals in sediments is that, as long as there are no other major ligands in the sediments, a metal will be in equilibrium with sulfide. The equilibrium will be based on the solubility product (Ksp) of that metal-sulfide (MeS). As such, the proportion of the metal that exist as free aqueous ion (Me^{2+}) is dependent on the Ksp and the sulfide concentration (Howards, 1992).

As the Me^{2+} concentration increases, MeS will exceed its solubility product which initiates the formation of MeS. The majority of metal sulfides in sediments are FeS and MnS, which have solubility products greater than some other more toxic metals such as Cu, Pb, Cd, Ni, and Hg (Table 1.1). As long as MeS is less soluble than iron monosulfide (FeS), FeS will be replaced by those toxic metals. Under equilibrium, the divalent metals (Me^{2+}) will displace the iron in FeS to form insoluble metal sulfide (MeS) and aqueous ferrous iron (Fe^{2+}). This reaction occurs quite rapidly and yields a solid metal sulfide product that is not bioavailable (Casas and Crecelius, 1994).

$$Me^{2+} + FeS \rightarrow MeS + Fe^{2+}$$

In general, one metal can be exchanged with another metal if its sulfide is less soluble than the metal sulfide already presents:

$$Cu^{2+} + ZnS \rightarrow Zn^{2+} + CuS$$

Whether precipitation takes place or not will depend on the availability of AVS. If metal concentrations exceed AVS concentrations, the binding ability of AVS will saturate and free metal ions can be found in the pore water.

Table 1.1 . Metal Sulfide Solubility Products (source : Di Toro et al., 1990)

Metal Sulfide	Common Name	log $K_{sp.2}$	log K_{sp}
MnS	Albandite	-0.40	-19.15
FeS (am)	Amorphous iron sulfides	-3.05	-21.80
FeS	Mackinawite	-3.64	-22.39
NiS	Millerite	-9.23	-27.98
ZnS	Wurtzite	-9.64	-28.39
CdS	Greenockite	-14.10	-32.85
PbS	Galena	-14.67	-33.42
CuS	Covellite	-22.19	-40.94
HgS	Metacinnabar	-38.50	-57.25

* Solubility products, $K_{sp.2}$, for the reaction : $Me^{2+} HS^- \leftrightarrow MeS(s) + H^+$

K_{sp} is for the reaction : $Me^{2+} + S^{2-} \leftrightarrow MeS(s)$

All logs are $\log_{10}$

1.3.5 Analysis of Pore Water Metals

According to the sediment study performed by Ankley and others (1991 and 1993), toxicity was not observed in sediment samples with SEM/AVS ratios greater than 1. It is an apparent contradiction to the hypothesis mentioned in the previous section. The data suggested the presence of other binding phases, such as organic ligands, for Cd, Ni and Cu in the tested sediments. On the other hand, the data also noted a correlation between sediment toxicity and Cd and Ni concentrations in the pore water. Evaluation of the concentration of Ni and Cd in the pore water provided a more accurate prediction on the occurrence of toxicity.

These studies have two implications. The first one is the importance of analysis of metals in pore water. The data available indicates that the evaluation of metal concentrations in pore water and SEM/AVS ratio can throw light on metal bioavailability in sediments. SEM/AVS ratio has been employed successfully to predict the absence of acute toxicity for Cd, Ni, Pb, Zn, and Cu. Metal concentrations in pore water are also useful in prediction of presence and the extent of metal toxicity in sediments. Analysis of metals in pore water is also useful in the prediction of the toxicity of those metals (As, Cr, Ag) that are not bounded by AVS. Moreover, the bioavailable fraction of metals is also predictable basing on pore water concentrations when AVS is oxidized in aerobic sediments (Ankley, et al., 1994; Pesch et al., 1995). Pore water analysis and SEM/AVS ratio are two complementary methods, therefore, both should be used to assess metal toxicity in sediments.

Secondly, these studies also indicate that the existence of other ligands, other than AVS, may change the apparent solubility products of metals in the natural systems. Therefore, a comprehensive study on different partitioning phases of metals can provide a better understanding on the role of AVS over other partitioning phases in controlling metal bioavailability in the study area.

1.4 SIGNIFICANCE OF THE RESEARCH

This study is significant in 3 major aspects : (1) importance of metal bioavailability studies in Hong Kong, (2) importance of AVS studies in Hong Kong, (3) the approach of the present study.

1.4.1 Importance of Metal Bioavailability Study in Hong Kong

The assessment of potential metal toxicity in aquatic environment has long been ignored in Hong Kong, although a wide range of physical, chemical and biological determinants has been monitored. Heavy metals being measured are in total amount, not the metals that are biologically available to the biota. Considering these findings, it is rather difficult to assess the potential effects of these toxicants. The studies of AVS and speciation of metals are most probably helpful in making

confirmatory conclusions on the availability of metals in the Hong Kong aquatic system.

This kind of study is especially important in an estuarine environment. In Hong Kong, a lot of untreated sewage effluents are discharged into the river channels, such as Shing Mun, Lam Tsuen and Tuen Mun Rivers. The metals discharged in these rivers will eventually empty into the sea. Many previous investigations suggested that the estuary, where large amounts of waste materials brought down by rivers meets the near-coast marine system, is the major problem area (Forstner and Wittmann, 1979). This merging zone between river and sea is the region with the most abrupt changes. Therefore, it is highly probable for metals to be remobilized to become available to the biota in this region. As a result, it is necessary to investigate the metal bioavailability in an estuarine environment.

1.4.2 Importance of AVS Study in Hong Kong

Previous studies have demonstrated a corresponding increase in biota mortality when molar ratio of metals to AVS exceeds 1. Hence, the relation between AVS and metals in the sediments has been recommended as a valid tool in the assessment of metal toxicity in the aquatic environment. Among all the metal binding phases, AVS is the key binding phase of heavy metals in anoxic sediments which are commonly found in the Hong Kong coastal areas. Even a small amount of AVS can sequester a significant quantity of metal (Di Toro, 1990). Therefore, the study of AVS in sediments is of great significance in Hong Kong.

On the other hand, AVS concentrations in aquatic sediments are closely related to a number of biogeochemical processes and thus will vary greatly. Apart from the spatial variation of AVS, it is a proven fact that concentration of AVS vary seasonally (Howard and Evans, 1993; Leonard, 1993). In Hong Kong, there is a remarkable seasonal variation in temperature and rainfall. The difference in average temperature between winter and summer is around 20°C. Hong's study (1992) speculated that when the environment contained more oxygen, organic matters and sulfide would be oxidized. Association with the oxidation is the adverse effects on the biota that caused by the released metals. Therefore, the formation of AVS and the circumstances under which they are formed and subsequently lost are of great importance to our sediment metal partitioning studies.

The present study is the first attempt in Hong Kong to sample and analyze the AVS concentration in the bottom sediments systematically. A study of AVS has a great theoretical implication and practical significance. In related theories, very little is known about the occurrence of AVS and its pattern of change in concentration, and hence the mediating role, in different seasons in Hong Kong. Therefore, one of the study objectives is to ascertain the pattern of the occurrence of AVS in bottom sediments and to apply the SEM/AVS ratio concept in the assessment of the potential toxicity of Hong Kong sediments. This will provide a new dimension for the Government to review the existing measuring scale of sediment quality and to formulate a cost-effective strategy for spoil management purpose.

1.4.3 Approach of the Present Study

Since the 1990's, the studies of AVS from a toxicological standpoint have verified the importance of AVS in mediating metal bioavailability in a controlled laboratory environment (Ankley et al., 1993; Ankley et al., 1994; Casas and Crecelius, 1994; Di Toro et al., 1992; Pesch et al., 1995). Even though there were other studies considering the effectiveness of the mediating role of AVS and variation of AVS concentrations, most of these studies were conducted in freshwater lakes (Howard and Evan, 1993; Leonard et al., 1993). Unlike previous studies, this research focuses on AVS in bottom sediments of a tidal inlet. The area covered by this study really stands out as a different hydrological environment that is calling for the attention of researchers.

Moreover, we have also adopted a different approach to study AVS. Besides the evaluation of the AVS concentrations in a tidal inlet and the role of AVS in metal toxicity mediation, study of metal speciation in the sediments and overlying water is also the focus of this study. Furthermore, the study has also compared the concentrations of SEM with the metal in total amount and fraction IV (metals bind to organic matters and sulfide) in order to further verify the role of AVS in metal toxicity mediation. With the data on metal concentrations and speciations in the overlying water and bottom sediments, as well as the understanding on the effectiveness of AVS in controlling metal bioavailability, this study can reconstruct the picture of metal bioavailability in the Shing Mun River and Inner Tolo Harbour.

1.5 ORGANIZATION OF THE THESIS

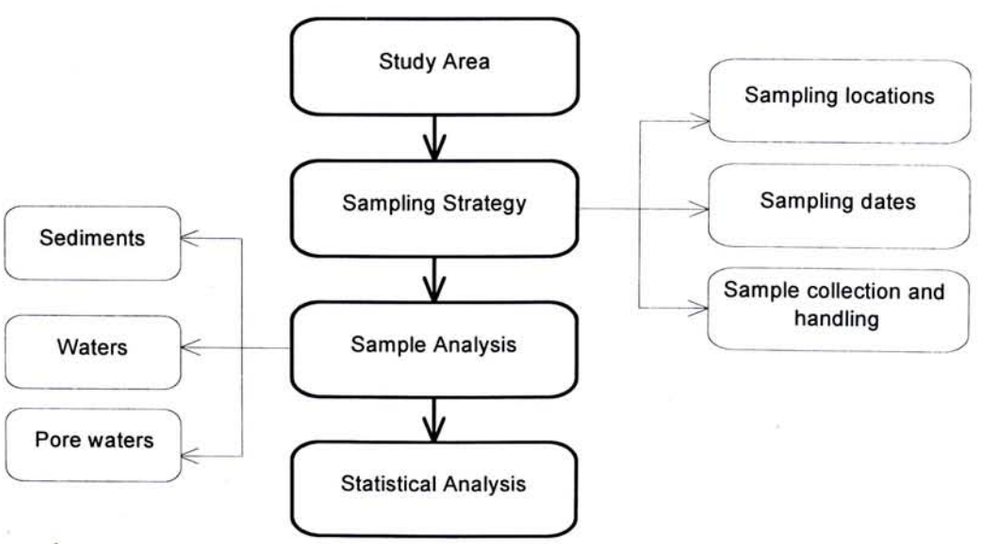
The methodology adopted in the study will be discussed in Chapter 2. Chapter 3 will outline the metal pollution in the overlying water and sediments of the study area and Chapter 4 will cover the speciation of metals in the water and sediments. This study will estimate the fraction of metals that are bioavailable in water and sediments and assess the probability of metal remobilization under the changes in water properties. It will focus on the variation of AVS and its role in controlling metal bioavailability and hence metal toxicity in chapter 5. In the chapter of conclusion, a comprehensive picture of the source, movement and bioavailability of metals in this study area will be given.

CHAPTER 2

METHODOLOGY

This chapter covers the methodology of this study. As a proper understanding of the background of the study area is a prerequisite for structuring an appropriate sampling strategy, this chapter begins with a description of the study area. It is followed by a detailed description of the sampling strategies in terms of sampling locations, sampling dates and sample collection methods. Methods for sample analysis in the laboratory and the statistical methods for data analysis will be illustrated in the last section of this chapter.

Figure 2.1. Framework of the Methodology



2.1 STUDY AREA

The study was undertaken in Shing Mun River which is a 50 Km river system running through Tai Wai, Shatin, Fo Tan and emptying into Inner Tolo Harbour (EPD, 1994b). Tolo Harbour is a semi-estuarine embayment in the northeastern quadrant of Hong Kong (Figure 1.1). Because of the "bottleneck" topography, the exchange of water in the Tolo Harbour with outside water is poor. This has been aggravated by the recent reclamation in Shatin and Tai Po which has further slowed down the tidal exchange rate. Not surprisingly, Tolo Harbour was regarded as the most polluted marine environment in Hong Kong (Morton, 1988). According to the EPD's report (1994a), the levels of Zn and Pb in the sediments of inner Tolo Harbour are comparable to those found in Victoria Harbour. Moreover, the building up of heavy metals in Tolo Harbour is even faster than that in Victoria Harbour (Yim and Fung,1981).

Besides Tolo Harbour, Shing Mun River and its tributaries (Fo Tan nullah, Siu Lek Yuen nullah and Tin Sum nullah) are also polluted. In the 1980's, Fo Tan nullah was heavily contaminated by unauthorized discharge of industrial effluents. The Siu Lek Yuen nullah, in the past, was suffering from pollution of livestock waste. Moreover, concentration of Al in the Tin Sum Nullah is comparatively higher than in other sampling stations as some contaminants from the former water treatment plants still remain in the nullah (EPD, 1994b). Lack of flushing has turned the channel from a drain to a sink for materials being brought downstream by the

river and upstream by the tides. With a continuous input of pollutants, Shing Mun River is classified as one of the "priority rivers" for clean up by EPD (EPD, 1994b).

Although there has been a significant reduction in Cu, Cr and Ni since the early 1990's, more recent monitoring results indicate that the trend of improvement has not been maintained. Some aspects of water quality are as bad as in 1988 (EPD, 1994b). Therefore, Shing Mun River and Inner Tolo Harbour provide an ideal environment for the study of metal pollution.

Whilst Shing Mun River is a tidal channel, it shares some characteristics of an estuary. Pitchard (1967) defined an estuary as "a semi-enclosed coastal body of water which has a free connection with the open sea and within which seawater is measurably diluted with freshwater from land drainage". The mixing zone between river and sea is a region with the most abrupt change among the natural systems (Forstner and Wittmann, 1979). The variation will in turn affect the metal remobilization and bioavailability in the study area.

2.2 SAMPLING STRATEGY

2.2.1 Sampling Locations

As mentioned before, the concentration of AVS may change from place to place under the influence of many factors. It is expected that AVS level varies along the channel, and so would the level of metal concentrations in sediments.

Based on these considerations, a number of sampling locations has been selected to represent the upstream, downstream and the Harbour estuary conditions. The distribution of sampling locations is shown in Figure 2.2.

These sampling locations can be categorized into 2 groups:

1. Along the main channel to the Inner Tolo Harbour.

   (Location 1, 2, 5, 6, 7, 9, 10, 11, 12)

   These locations are expected to provide information on the origin of metal input, as well as information on variations in the concentration of AVS and metals along a channel-to-sea profile.

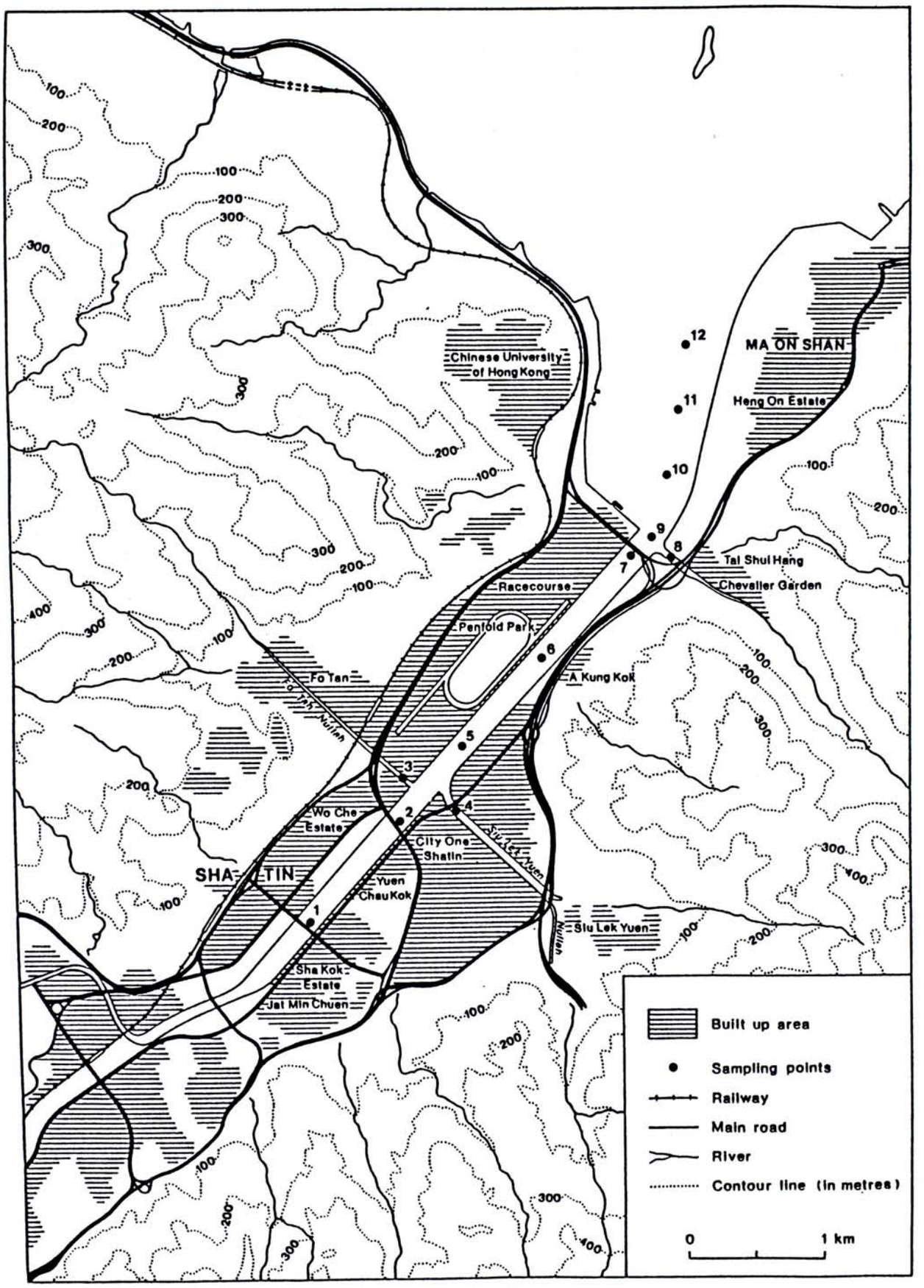
2. At the junctions of the tributaries with the main channel.

   (Location 3, 4, 8)

   These locations are used to ascertain the concentration of metals and AVS in the tributaries, before they join the channel main.

On each sampling trip, these sampling locations were located with a prismatic compass by referring to three fixed prominent landmarks. As it was not always possible to return to the exact position of the original sampling site, some minor error in positioning was inevitable. However, this may not be deleterious to the results as repeated sampling at the same location all year round may eventually alter sediment stratigraphy at that location.

Figure 2.2. Distribution of Sampling Locations in the Study Area



2.2.2 Sampling Dates

As this study aims at studying the temporal variation of the concentration of metals and AVS, a sampling program covering different seasons was worked out. Concentration of AVS is believed to be maximum in summer under an optimum sulfate reduction rate in warmer seasons and to be minimum in winter through oxidation. This variation should be especially prominent in Hong Kong because there is a remarkable change in water temperature between the seasons. Moreover, heavy rainfall in summer is another climatic factor affecting the AVS concentration.

Because of time and resource constraints, sampling could only be carried out on a seasonal basis (i.e., every 3 month). The exact dates of sampling were 27 March 1995, 8 July 1995, 6 October 1995 and 15 December 1995, representing spring, summer, autumn and winter, respectively.

2.2.3 Sample Collection and Handling

Samples of bottom sediments, overlying water and pore water were collected at each sampling location in the four seasons to yield the data required for reconstructing the pattern of AVS variation and the speciation of metals in the study area. Because both sulfide substances and trace amount of metals can change rapidly after sampling, extra care was taken to minimize any error arising from sample collection and handling.

As there is no standard method for the sampling of AVS, a sampling protocol had been worked out for the present study. It was decided a *priori* that the sediment layer to be sampled should include the majority of the AVS plus the biologically active zone, and should be most sensitive to seasonal changes. Based on these considerations, a sampling depth of 15 cm was adopted.

A Brige-Ekman grab sampler with a cutting height of 15 cm was used for sediment collection. This small lightweight sampler was chosen because of the ease of handling. Experience gained from other research projects also showed that this sampler is suitable for sampling soft fine-grained sediments (Mudroch and MacKnight, 1991), such as the mixture silt and sand, commonly found in the marine sediments of Hong Kong. However, large objects such as gravel and shells could be caught between the jaws, sometimes making sampling difficult.

In addition to the variation in space and time, AVS is also known to vary with depth to reflect the variability of iron, organic material, sulfate and other physical properties. To gain some insight into the vertical variation, some sediment cores were collected by a Kajak-Brinkhurst (K-B) corer in autumn. After sampling, the cores were immediately capped at both ends to reduce oxidation. However, no core could be obtained at locations 3, 8, and 9 because the sediments were either too coarse or too thin for coring.

In addition, 3 replicate cores were collected at location 2 to ascertain the representatives of the collected core samples. It is generally assumed that repeated

sampling would be very close to the initial sampling location. Replicate sampling can throw some light on errors in field sampling.

From each core sampled, 4 subsamples were obtained and measured for its AVS concentration (μmol/g), pH, Eh (mv), sediment colour and grain size. The results are listed in Table 2.1. It can be seen that the characteristics of core no. 2 and no.3 are similar to each other, but are obviously different from core no.1.

Table 2.1. Comparison of 3 Sediment Cores Collected at Sampling location No.2

Depth	AVS (μmol/g)			pH			Eh(mv)		
(cm)	Core 1	Core 2	Core 3	Core 1	Core 2	Core 3	Core 1	Core 2	Core 3
5	55.58	152.40	172.05	8.02	7.72	7.91	-373	-338	-354
10	40.73	64.75	69.78	7.94	7.87	7.96	-387	-394	-366
15	108.11	----	----	7.9	----	----	-386	----	----
20	277.76	58.11	121.87	7.85	8.22	8.15	-355	-395	-330
29	----	107.99	92.30	----	7.82	8.16	----	-392	-319

Table 2.2. Significance Level of ANOVA Test on Variation of Selected Sediment Properties in Three Sediment Cores Collected at Sampling Location No.2

Variables	Between Cores	Between Depths
AVS (μmol/g)	> 0.05	> 0.05
pH	> 0.05	> 0.05
Eh (mv)	> 0.05	> 0.05

However, neither the variations between cores nor between depths were statistically significant (Table 2.2). Therefore, it can be concluded that variation of sediment characteristics in a small area is within an acceptable range. In other words, a single replicate can represent each sampling location.

Overlying water samples were also collected at each sampling location because the chemical properties of sediments are influenced by the chemistry of its overlying water. The properties of the overlying water also provide information on the hydrological condition of the study area. During each sampling trip, pH, redox (Eh), salinity, temperature, dissolved oxygen (DO) and turbidity were measured and recorded on the boat by lowering the sensors into the water at 0.5 m intervals.

Water samples were also collected from the surface and bottom portion of the overlying water by a 2-L horizontal water sampler. The bottles were filled completely to reduce oxidation. All sample containers were thoroughly cleaned with laboratory detergent, tap water, 10% nitric acid, and deionized water.

After sampling, sediments and water samples were placed on ice and transported back to the laboratory. On arrival, the sediment samples were put into a nitrogen-purge glove box for separation and homogenization immediately. Both sediment and water samples were refrigerated at $4^{o}C$ awaiting for analysis.

Pore water analysis is another important component of the study. It was obtained by placing the wet sediments in a 250 ml centrifuge bottles and centrifuged

at 4°C for 20 minutes at 5,000 rpm. The extracted pore water was filtered before further analysis.

Centrifugation followed by filtration was considered to be having an effect similar to *in situ* dialysis (Carignan et al., 1985). Schults and others (1992) also concluded that centrifugation produces a lower coefficient of variance for the replicates than the dialysis method. Ankley and others (1991a) suggested there is a loss of heavy metals during filtration owing to the oxidation by oxidized metal-ligand or absorption on the filter. However, if filtration has not been done, the residual particles in the pore water can cause errors in 2 ways. Firstly, the particles can cause interference in analytical procedures due to tube clogging. Secondly, if particles were allowed to remain in solution, heavy metals absorbed onto the particles would be analytically deemed to be the heavy metal concentrations in the pore water.

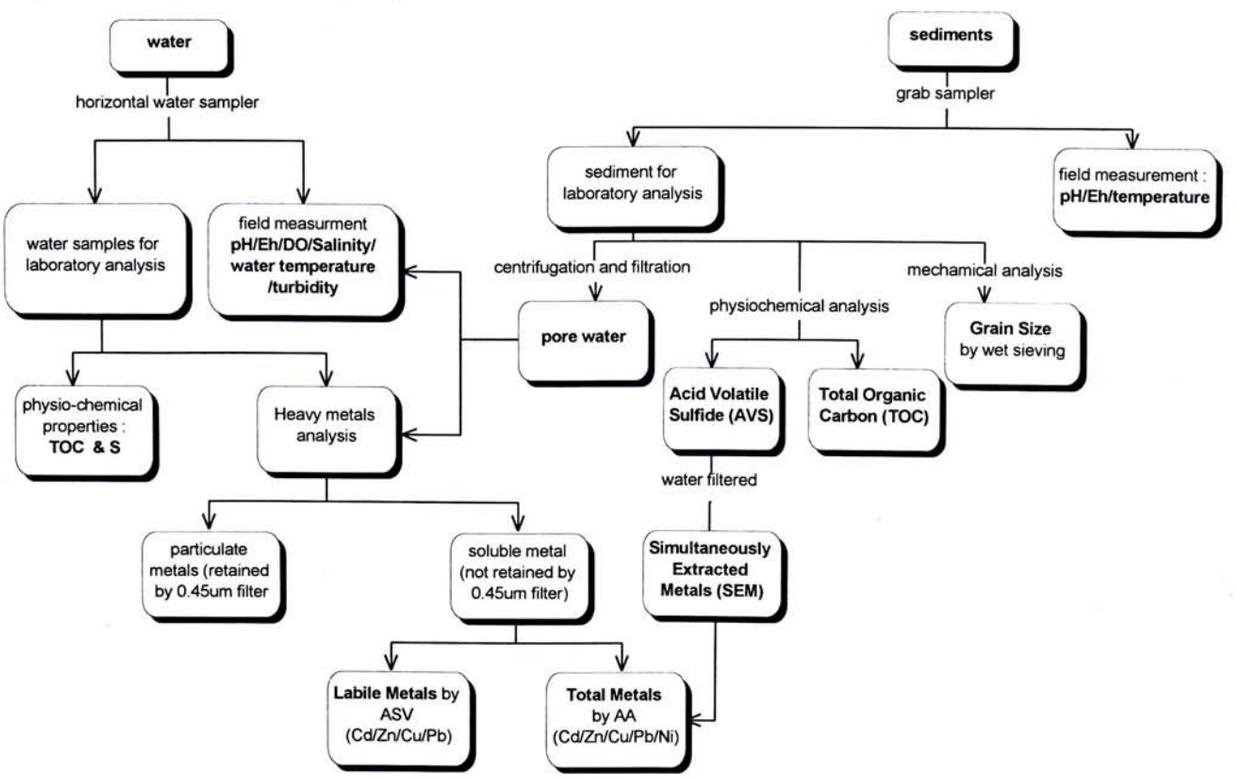
2.3 SAMPLE ANALYSIS

This section briefly outlines the analytical methods employed in the laboratory for sample characterization. The analytical framework is illustrated in Figure 2.3.

2.3.1 Sediment Analysis

pH, Eh and temperature of sediments were measured in field, while other physical and chemical determinants were measured in the laboratory. Physical (mechanical) analysis of the sediments refers to the grain size analysis by wet sieving method. AVS, SEM, total carbon (TC) and speciation of metals were also determined. All the determinants, other than the AVS, SEM and speciation of metals, were measured with reference to standard methods. There was some modification on the methods commonly used for the determination of AVS and the sequential extraction of metal speciation, and details of the new working procedures are listed in Appendix A and Appendix B respectively. Since storage may result in changes of AVS concentration, most of the analysis was performed within 48 hours and the metal speciation analyses were normally carried out within a week.

Figure 2.3 : Flow chart of analysis parameters



2.3.2 Pore Water and Overlying Water Analysis

pH and Eh of all these water samples were analyzed by the same method as used in the sediment analysis. Other parameters measured were conductivity, dissolved sulfide and TOC. Furthermore, measurement of the dissolved oxygen (DO) and turbidity of the overlying water was performed in the field.

With the limitations in time and resources, only those parameters that are either directly related to occurrence and speciation of metals, or to the formation of AVS were determined. The rationales for selecting those determinants and the methods of analysis are listed in Table 2.3. Further details are given in Appendix C.

Table 2.3. List of Analytical Methods Used and the Rationale for Determinants Selection

Determinants	Methods (sources)	Rationale for Selection
pH	Electrode method (manufacturer's manual)	pH value is the negative normal logarithm of the hydrogen ion activity which may have a bearing on the solubility and speciation of metals which in turn control bioavailability of metals
Eh	Electrode method (manufacturer's manual)	Eh is another major factor controlling the chemical process in nature, especially influencing on the valence of metals and their chemical compounds. It also indicates whether it is an oxidizing or reducing environment which in turn implicates the formation of sulfide.
DO	Direct measurement with DO probe and meter (manufacturer's manual)	Similar to Eh, it indicates the influence of the aquatic environment on the valence of heavy metals and their compounds. The concentration of sulfide in water or on surface sediments also depends on the DO level of the overlying water.

Turbidity	Direct measurement with Turbidity probe and meter (manufacturer's manual)	Turbidity is expressed in suspended solids. It controls the amount of labile metals through the process of adsorption, precipitation, coprecipitation, etc.
Salinity	Direct measurement with Conductivity /Salinity probe and meter (manufacturer's manual)	Salinity is the total parameter for dissolved and dissociated substances. Not only can it indicate the occurrence of stratification in overlying water, but it can also indicate the degree of tidal and oceanic influence on the study area. Salinity also reflects the concentration of sulfate (AVS controlling factor) in the overlying water.
TOC / TC	Combustion-infrared method (Rump and Krist, 1992)	TOC provides a speedy and convenient way of estimating the degree of organic contamination. It is a controlling factor for the formation of AVS as it is needed in bacterial reduction of sulfate to sulfide. It is also another ligand to control metal bioavailability.
Dissolved S^{2-}	Mthylene Blue method (Rump and Krist, 1992) Electrode method (manufacturer's manual)	Dissolved sulfide may control the bioavailability of metals in the water column. It is also a component of the total acid volatile sulfide (AVS).
AVS	Purge and trap method (Allen et al., 1991; Allen et al., 1993) Diffusion method (Brouwer and Murphy, 1994) Electrode method (manufacturer's manual) Iodometric method (Rump and Krist, 1992)	AVS is the subject matter in the study owing to its primacy in mediating metal bioavailability.
SEM	Flame Atomic absorption spectrophotometric method (manufacturer's manual)	SEM is the amount of metals associated with AVS. By referring to SEM/AVS molar ratio, the level of metal toxicity, from high to low, can be distinguished.
Labile Metals	Anodic stripping voltammetric method (manufacturer's manual)	Labile metals are the most unstable form of metals in the aquatic system. Since they are easily uptaken by aquatic life, labile metals are regarded as the most toxic and bioavailable metals.

Total Metals	Flame and Furnace Atomic absorption spectrophotometric method (manufacturer's manual)	Summation of metals partitioning with different binding phases.
Speciation of Metals	Sequential extraction method (Tessier et al., 1979) Flame and Furnace Atomic absorption spectrophotometric method (manufacturer's manual)	Metal speciation study can show the chemical forms of metals present in sediments. It may show the probability of metal remobilization.
Grain Size	Wet Sieving Sediments pretreated with Calgon and NaOH, and mechanical stirring (Christie, 1987)	Sediment grain size has influence on the formation of AVS and the total metal concentration in sediments. The fraction <63μm was measured.

2.3.3 Limitations

Methods for assessing the relative bioavabilability of sediment-bound metals to benthic species can be grouped into three categories:(1) laboratory experiments, (2) field experiments and (3) field surveys of sediment characteristics and metal burden in indigenous benthic species (Campbell and Tessier, 1989). This dissertation only examines the relationship between the partitioning of heavy metals in the sediments and their potential bioavailability to the aquatic life. No bioassay was taken in the research. Therefore, this study only focuses on the metal concentrations in the aquatic environment. The biochemical processes occurring inside the organisms are outside the scope of this study.

The time and equipment constraints also lead to several problems in sample analysis. These problems include the delay of sample measurement, insufficient temporal replication, analytical error, and the representative of the results.

Firstly, there has been some delay in the analysis of sediment samples. With a total of 12 sediment cores, the amount of work involved in AVS analysis is quite substantial and could only be finished within a week, instead of 48 hours, after collection. However, this should not affect the validity of the results as the work of Boothman and Helmstetter (1992) quoted in Leonard et al. (1993) indicated that sediments could be stored in either frozen condition or refrigerated without a nitrogen atmosphere for up to 10 days without loss of AVS.

Furthermore, the temporal replication of the sampling may not be comprehensive enough to reveal the seasonal variation patterns. The large spatial variation of AVS in the tidal inlet region may also compound the temporal variation of AVS. Therefore, 2 solutions are suggested for future studies. The first is to consider each occasion of sampling as unique, rather than as a replicate used in estimating the mean and variance for longer time-periods of interest. Alternatively, a sampling schedule incorporating systematic replicated sampling times at different temporal scales and with spatial replication appropriate to the spatial scale comparison (Morrisey et al., 1994)

In addition to the problems in sampling, limitations were also found in sample analysis. First of all, data of TOC in the sediments was not available. The

total organic carbon analyzer measured the carbon content by combustion at 760°C. Because CO_2 can also be released from inorganic carbon sources, the results obtained only showed the total carbon rather than the merely organic carbon content of the sediments.

Besides, the detection of Pb in sea and pore water with Atomic Absorption Spectrophotometry (AAS) was usually interfered by the matrix in the seawater. Therefore, the range and variation of Pb were great among the samples.

Furthermore, it was surprising to know that the concentration of labile Zn exceeds the total amount of Zn in the overlying water and pore water samples. However, such differentiation did not exist in Cd, Cu, and Pb. Since the samples in the two analyses were subjected to same pretreatment process and the similar detection limits of the machines, the exact reasons for such findings remained undefined.

Limited by the time and resources, the number of replicates that could be measured was somewhat restricted. In the study, most of the analytical results were based on the measurement of 1 sample. Therefore experimental error may appear in the final results. Every attempt was made to minimize the human error, but the errors arisen as a result of the limitation of the equipment was inevitable.

2.4 STATISTICAL ANALYSIS

Statistical analysis was performed with procedures in the Microsoft Excel package. The statistical analysis that was employed to deal with the results of sediment, overlying water and pore water samples included one-way analysis of variance (ANOVA), correlation analysis. Statistical significance was assessed at a 5% significance level ($p \leq 0.05$).

CHAPTER 3

HEAVY METALS IN WATER AND BOTTOM SEDIMENTS

Rapid industrial development in Shatin and Tai Po close to the Tolo Harbour has created Hong Kong's most critical marine environmental problem. The high metal concentration in the sediments of inner Tolo Harbour (EPD, 1994a) is a result of the indiscriminate discharge of large amount of metal-containing industrial effluent into the harbour through the channel. Before evaluating the potential risks that posed by the heavy metals in the sediments, it is instructive to examine the metal contents both in the water column and the bottom sediments.

3.1 METALS IN THE WATER

As described in Chapter 2, surface and bottom water samples were collected at the twelve sampling locations in each of the four seasons. The seasonal and annual averages of various metals are presented in Table 3.1. In this chapter, the concentration refers to the "total" concentration, composed of the labile and non-labile fractions. Likewise for sediments, "total" concentration refers to the sum of 5 sequentially extracted species.

3.1.1 Variation of Metal Concentrations

The data in Table 3.1 seem to suggest that Zn is the most abundant metal ion in the overlying water and it is followed by Cu, Pb, Ni and Cd. Moreover, the results also suggest the existence of seasonal differences in metal concentration. An ANOVA test was undertaken to ascertain if such differences are significant and the results show that except for Pb, there are significant seasonal differences in the concentrations of all metals (Table 3.2). In general, metals are higher in spring and winter than in summer and autumn. It cannot be ascertained if the seasonal differences are due to the dilution effect of rainfall in summer and autumn.

Table 3.1. Seasonal Mean and Range of Metal Concentrations in the Overlying Water

Seasonal Mean	Zn (μg/l)		Cd (μg/l)		Pb (μg/l)		Cu (μg/l)		Ni (μg/l)	
	S	B	S	B	S	B	S	B	S	B
Spring	560.6	533.8	4.0	3.6	23.6	20.2	37.2	36.3	2.7	3.1
Summer	190.0	203.8	0.8	0.7	9.5	41.0	31.6	37.2	4.6	5.5
Autumn	239.5	264.6	0.4	0.4	22.6	39.3	13.8	24.6	5.4	6.9
Winter	354.7	261.2	1.8	1.5	29.2	21.8	25.1	32.9	13.6	13.9
Annual Mean	336.2	315.9	1.75	1.55	21.2	30.8	26.9	32.8	6.6	7.4
Annual Range	190.0-560.6	203.8-533.8	0.4-4.0	0.4-3.6	9.5-29.2	20.2-41.0	13.8-37.2	24.6-37.2	2.7-13.6	3.1-13.9

* S = Surface Water B = Bottom Water

Table 3.2. Significance Level of ANOVA Test on Seasonal Variation of Metals in the Overlying Water

Metals	Significance Level	
	Surface Water	Bottom Water
Zn	0.001	0.001
Cd	0.001	0.001
Pb	> 0.05	> 0.05
Cu	0.001	0.001
Ni	0.001	0.001

As regards the spatial variation of metal concentrations at various sampling locations, the data (Table 3.3) do not suggest any specific trend of increase or decrease from the upstream to the downstream direction.

Table 3.3. Spatial Mean and Range of Metal Concentrations in the Overlying Water

sampling location	Zn (μg/l)		Cd (μg/l)		Pb (μg/l)		Cu (μg/l)		Ni (μg/l)	
	S	B	S	B	S	B	S	B	S	B
1	432.3	285.0	2.7	2.2	27.8	28.5	27.7	33.6	11.4	7.2
2	287.0	414.3	2.2	1.4	9.9	7.7	26.3	29.3	8.5	3.8
3	287.3	333.3	1.7	1.5	13.6	14.9	24.0	31.5	5.3	4.7
4	267.0	238.3	1.8	1.9	31.0	21.6	23.4	29.6	4.5	6.2
5	317.5	273.3	1.6	1.6	14.5	21.8	22.2	30.0	4.1	10.9
6	518.5	270.3	1.5	1.5	32.8	31.0	25.0	37.2	5.8	6.9
7	324.5	267.3	1.1	1.6	20.8	40.6	27.7	33.3	4.9	5.0
8	299.3	309.0	1.4	1.4	16.5	14.8	25.3	30.9	4.1	8.1
9	309.0	453.0	1.8	1.7	19.7	60.8	27.8	34.7	5.7	7.3
10	281.8	310.0	2.1	1.6	40.4	53.4	32.6	32.3	5.2	12.5
11	347.5	301.8	2.2	1.0	13.3	33.6	29.8	32.8	10.9	3.1
12	362.8	335.0	0.9	1.6	14.7	38.7	31.4	38.0	8.5	9.8
Mean	336.2	315.9	1.8	1.6	21.3	30.6	26.9	32.7	6.6	7.1
Range	267.0-518.5	267.3-453.0	0.9-2.2	1.0-2.2	9.9-40.4	7.7-60.8	22.2-32.6	29.3-38.0	4.1-11.4	3.8-12.5

* S = Surface Water B = Bottom Water

On the differences in metal contents between the surface and bottom water (Tables 3.1 and 3.3), only Cu has been found to be significantly different under ANOVA test. Concentration of Cu is higher in bottom water than the surface water. The differences of other metals in the water column are statistically insignificant (Table 3.4).

Table 3.4. Significance Level of ANOVA Test on Difference of Metals between the Surface and Bottom Water Layers

Metals	Significance Level
Zn	> 0.05
Cd	> 0.05
Pb	> 0.05
Cu	0.01
Ni	> 0.05

3.1.2 Metal Pollution Level of the Overlying Water

Table 3.5 compares the average metal concentration of this study with those of earlier ones and a number of interesting points can be identified. Firstly, the concentrations reported by EPD in 1994 are significantly lower than findings of this study. Secondly, the metal concentrations of the study area are higher than the average metal contents of Hong Kong marine water in 1974. Lastly, most metals are many times higher than the average seawater composition (Morre and Harriss,1974).

Table 3.5. Comparison of Metal Contents in the Study Area with Results of Others Research

	Metals (μg/l)				
	Zn	Cd	Pb	Cu	Ni
Study Area	326.0	1.7	11.4	28.8	19.7
Average Seawater Composition	12.3	0.1	0.1	2	---
Shing Mun River, EPD, 1994b	10	0.5	3.0	2.5	---
Tsuen Wan, Kwok, 1993	20.0	---	7.1	69.0	12.2
Average of Hong Kong Water, Morre and Harriss, 1974	0.09	0.05	0.66	0.07	---

*Average Seawater Composition: Morre and Harriss, 1974
Metal contents in Shing Mun Main Channel: EPD, 1994b
Average values of heavy metals in Hong Kong seawater: Morre and Harriss, 1974
Metals in marine water collected from Tsuen Wan (industrial area): Kwok, 1993

Some explanations can be advanced to account for the phenomena observed. The higher metal concentrations obtained in this study reflect a deteriorating trend of Hong Kong marine waters in the last two decades, and also the proximity of the Shing Mun River to the Fo Tan Industrial Estate in Shatin. In comparison with other similar studies, it can be seen that the concentrations of Zn, Pb and Ni are also much

higher in Shing Mun River than in Tsuen Wan Bay which is also polluted by another industrial source. This probably also reflects the weak tidal movement in the study area, which are unable to dilute the metals in the industrial effluent.

3.2 METALS IN BOTTOM SEDIMENTS

The high level of metals in the water is also echoed by high metal contents in the sediments. This section focuses on the concentrations and source of metals, as well as their variations. Table 3.6 and 3.9 shows the mean concentration of various metals at each sampling location and in each season, together with the coefficient-of-variation which is an indicator of degree of variability of the metal concentration. The result will also be compared with those of previous studies.

3.2.1 Spatial Distribution Pattern of Heavy Metals

As previously said (Table 3.1), Zn is the most abundant metal ions in the overlying water, it is also the dominant metal in the sediments. Besides Zn, considerable amount of Cu and Pb are also present. However, Ni and Cd exist only in smaller amount (Table 3.6). In general, metal concentrations are generally higher in upstream area (e.g. locations 1, 2 and 3) than near the estuary (e.g. locations 8, 9 and 10).

Table 3.6. Spatial Variation of Metal Concentrations (μg/g) in the Marine Sediments

	Metals (μg/g)				
Locations	**Zn**	**Cd**	**Pb**	**Cu**	**Ni**
1	357.8	2.3	107.5	58.2	16.0
2	362.3	2.6	105.6	106.0	19.8
3	487.7	1.6	114.4	231.4	27.3
4	157.4	1.0	42.6	34.8	6.2
5	283.8	1.7	88.3	80.5	13.9
6	219.2	1.6	84.1	91.1	16.4
7	217.5	1.5	77.1	63.7	13.9
8	51.5	0.2	22.8	11.0	2.5
9	80.5	0.5	32.8	16.1	4.5
10	103.5	0.6	50.0	37.2	7.5
11	170.2	1.4	62.9	105.9	18.7
12	138.8	1.0	59.3	55.0	11.7
Mean	218.3	1.3	70.6	74.2	13.2
C.V.	0.69	0.60	0.45	0.87	0.59

* C.V. = Coefficient of Variation

Table 3.7 Metal Concentration in the Industrial Effluent Discharged by Various Industry in Tsuen Wan (Source: Lam, 1992)

Industry		Cr mg/l	Cu mg/l	Ni mg/l	Pb mg/l	Zn mg/l
Electroplating	min	0.1	0.1	0.1	0.1	0.1
	max	400	900	1400	500	250
Electronics	min	-----	0.5	0.1	0.1	0.1
	max	-----	3000	130	3	10
Textile	min	0.1	0.1	0.1	0	0.5
	max	10	2	0.5	0	0.1

The variation in metal concentrations along the river can be attributed to a number of factors, namely the proximity to pollution source(s), the sediment grain size and the organic carbon contents. Proximity to the pollution source is of dominant importance as the closer the sampling location is to the source, the higher will be the metal contents. Amongst the various sampling locations, location 3 has

the highest concentrations of Cu, Ni and Zn. This sampling location is just next to the Fo Tan Industrial Estates where there are many electronic and metal plating industries. In Hong Kong, effluents from such industries (Table 3.7) are known to contain elevated levels of the metals mentioned (Hong, 1992; Lam, 1992).

Table 3.8. Correlation between Total Carbon, Sediment Grain Size and Metal Contents

	Total Carbon	Grain Size
Total Carbon	1	
Grain Size	0.59*	1
Zn	0.56*	0.37*
Cd	0.68*	0.59*
Pb	0.69*	0.47*
Cu	0.44*	0.24
Ni	0.60*	0.44*

*significance level of the correlation is < 0.05

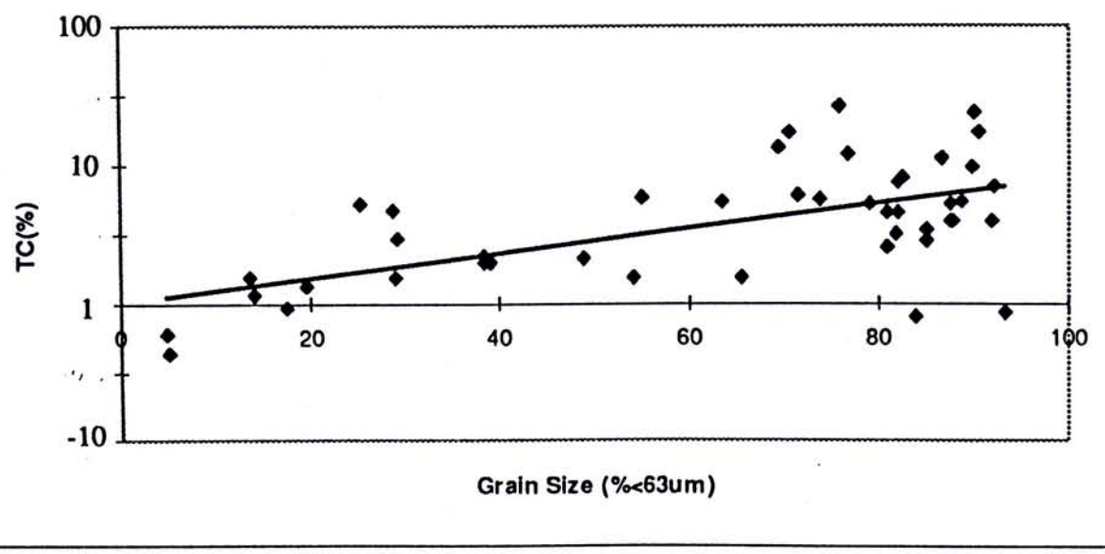
Grain size is another factor affecting metal concentrations in the bottom sediments. In the study area, a marked difference in grain size between upstream and downstream sampling locations has been observed. Upstream sediments are composed mainly of clay and fine silt, while sand is the dominant component near the estuary (Appendix F). Heavy metals are mainly associated with fine silt and clay rather a with the coarser sediments because finer particles have a larger surface area and greater affinity for metals (Groot et al., 1982; Krumgalz, 1989; Salmons and Forstner, 1984). Furthermore, as coarser sediments are made up of quartz and other minerals that are low in heavy metal contents. Therefore, higher metal

concentrations are found at sampling locations dominated by fine grain material and they are mostly found in the upstream area.

Another important factor affecting the variation of metal concentrations is organic matter (Table 3.8) as metals can be bound on the humic and fluvic acid organic commonly found in the bottom sediments (Jonasson, 1977).

Like some other studies (Lin, 1990), a close inverse relationship between organic carbon and grain size can be found in this study (Figure 3.1). The smaller the grain size, the higher the concentration of the organic carbon. Since organic carbon is also related to grain size, high metal contents are usually found at locations where the sediments are fine and the organic carbon is high. These locations of high metal content are usually in the upstream area.

Figure 3.1. Correlation between Grain Size and Total Carbon (Corr = 0.59)



3.2.2 Temporal Variation of Metal Content in the Bottom Sediments

The data shown in Table 3.9 seem to suggest some variations of metal concentrations in different seasons. The concentrations are particularly low in autumn and winter. The low concentration can be attributed to the change in the surficial materials in the channel and sea bottom that brought about by the scouring effect of the summer storms and the subsequent deposition of fresh materials on the metal-laden sediments. However, the seasonal variations in metal concentration cannot be established by the analysis of variance (Table 3.10).

Table 3.9. Seasonal Variation of Metal Concentrations (μg/g) in Marine Sediments

	Metals (μg/g)				
Season	**Zn**	**Cd**	**Pb**	**Cu**	**Ni**
Spring	246.8	1.5	76.9	94.7	15.7
Summer	279.0	2.2	85.0	102.3	16.8
Autumn	186.3	0.7	64.3	52.0	10.8
Winter	191.5	1.1	64.3	56.9	11.2
Mean	225.9	1.4	72.6	76.5	13.6
C.V.	0.20	0.46	0.14	0.34	0.23

*C.V.= Coefficient of Variation

Table 3.10. Significance Level of ANOVA Test on Seasonal Variations of Metal Concentrations (μg/g) in Bottom Sediments between Seasons

Metal	**Significance Level**
Zn	> 0.05
Cd	> 0.05
Pb	0.001
Cu	> 0.05
Ni	> 0.05

3.2.3 Metal Pollution Level of the Bottom Sediments

To answer the question of whether metal contents in the bottom sediments in the study area are more contaminated than those in other parts in Hong Kong and other places in the world, some figures have been tabulated for comparison (Table 3.11)

Table 3.11. Comparison of Metal Concentrations (μg/g) in the Bottom Sediments at Different Location

		Metals (μg/g)				
Location	**Landuse**	**Zn**	**Cd**	**Pb**	**Cu**	**Ni**
Study Area : mean	mixed landuse	218.3	1.3	70.6	74.3	13.2
: range		22.5-110.5	0.2-3.8	11.8-171.0	4.6-507.6	2.2-41.7
♣Global Standard	fossil shales	95	0.2	20	45	68
*Victoria Harbour	mixed landuse	115-528	11-18	162-367	77-6665	32-212
#Chek Lap kok	harbour	73.4	---	68.7	68.7	31.3
#Lamma Island	harbour	193.1	---	70.4	65.4	45.5
#Central	commercial	153.1	---	32.3	175	27.2
#West Kowloon	industrial	474.1	---	1180.6	141	34.9
#Kowloon Bay	industrial	461.2	---	182.1	1296	150.3
#Tsuen Wan	industrial	317.0	---	159.0	889	155.0

Source:
*Hong, 1992 (range of metal concentrations)
#Kwok, 1993 (mean metal concentrations)
♣Turekian and Wedepohl (1961) cited in Salomons and Forstner (1984)
(All the locations are shown in Figure 1.1)

The metal concentration in the bottom sediments of the study area is apparently much higher than that in the fossil shales, reported by Turekian and Wedepohl (1961) which was cited by Salomons and Forstner (1984), as a global

basis for comparison of metal contaminated sediments (Table 3.11). The high metal contents in the study area suggest the input of metals into the aquatic system from anthoropogenic sources. Within the territory of Hong Kong, the bottom sediments in the study area are not as heavily polluted as those close to other industrial areas, such as West Kowloon, Kowloon Bay and Tsuen Wan. In fact, the levels of some metals in the study area are close to those found at less polluted areas in southern Hong Kong (e.g. Lamma Island). However, this is not to say that the bottom sediments in the study area are not contaminated. Actually, metals are not evenly distributed, the metal contents at some sampling locations in the upstream are as high as the most polluted areas of Hong Kong, such as Tsuen Wan and Kowloon Bay.

3.3 CONCLUSION

The study area suffers from quite serious metal pollution. Elevated level of metals is found in the channel water suggesting a continuous input of metal pollutants. Although sediments in the study area are not as heavily polluted as other industrial areas in Hong Kong, relatively higher metal levels are found in the upstream area of Shing Mun River. Nevertheless, data that have been presented so far are the concentration of various metals in total amount rather than the different chemical speciations. Whether the metals create any significant risk to the human and biological population depends on the forms that these metals exist. This issue will be examined in the next chapter.

CHAPTER 4

SPECIATION OF METALS IN THE OVERLYING WATER AND BOTTOM SEDIMENTS

As the aquatic system supports a large and diverse assemblage of organisms, ascertaining the amount of metals that are bioavailable, rather than the total metal contents, is obviously a crucial issue. It has been stated in the very beginning of this dissertation that metals which exist in different speciations exhibit different toxicity. Accordingly, the measurement of metal concentrations alone cannot accurately reflect the harmful impacts of the metals on the environment. Study of metal speciations in the overlying water and bottom sediments is needed to identify the fraction of metals that is bioavailable to the biota.

4.1 SPECIATION OF METALS IN THE OVERLYING WATER

Trace metals occur in seawater only in very low concentrations due to their rapid and efficient removal in the water column through adsorption, precipitation, and incorporation into biogenic particles (Libes, 1992). Through these processes, heavy metals remaining in the water column may exist in many different chemical forms (i.e., speciations). The sum of these forms contributes to the "total metals" of the water bodies, while the proportion of trace metals which stay in the overlying

water as free ions or loosely adsorbed on solids is commonly known as the "labile fraction".

It is generally accepted that uptake of metals by animals from a solution is more efficient than uptake directly from particulate materials (Luoma, 1989). Therefore, the main route for accumulation of trace metals in organisms is through the uptake of dissolved metals. In other words, labile metals in overlying water are more toxic than particulate, complexed and other form of metals. Knowledge of the labile metal concentrations and their quantity in the total is very important in assessing metal bioavailability.

4.1.1 Concentration of Labile Metals in the Overlying Water

The mean and range of labile metal concentrations in the overlying water are shown in Table 4.1. Among the metals analyzed, Zn is the most abundant labile metal ion in the overlying water, occurring at concentrations over 300 μg/l. The abundance of Zn can be explained by a number of factors. Firstly, Zn is a major component of the industrial effluent (Table 3.7). Secondly, Zn has a relatively lower affinity for clay, organic matters and dissolved sulfide (Di Toro et al., 1990; Jonasson, 1977; Mitchell, 1964). Therefore, Zn is less likely to be removed from the water column and even if it has been removed, it has a propensity to be remobilized.

Cu is the second most abundant labile metal ion in overlying water with a mean concentration around 5-6 μg/l. The concentration for labile Pb in the

overlying water is low, as Pb is normally precipitated as $PbCl_2$ at the normal pH of seawater (Babukutty and Chacko, 1995). Like Pb, the concentration of labile Cd is not notably elevated in bottom and surface waters.

Regarding the differences of labile metal concentrations between the surface and bottom water, labile metal concentrations are apparently greater in surface water than that in bottom waters. However, such differences are rather small and are not of statistical significance (Table 4.2). The results infer the lability of metals is relatively uniform in the water column.

Table 4.1. Mean and Range of Labile Metals (μg/l) in the Overlying Water

Labile Metals	**Surface Water**		**Bottom Water**	
	Mean	**Range**	**Mean**	**Range**
Zn	343.1	176.3 - 810.3	335.7	164.7 - 850.3
Cd	0.3	0.0 - 2.6	0.1	0.0 - 0.6
Pb	3.7	1.5 - 11.8	3.3	1.8 - 9.2
Cu	6.0	0.0 - 27.2	5.5	0.0 -50.4

Table 4.2. Significance Level of ANOVA Test on Variation of Labile Metals between Water Layers

Labile Metals	Significance Level of the Variation between Water Layer
Zn	> 0.05
Cd	> 0.05
Pb	> 0.05
Cu	> 0.05

4.1.2 Seasonal and Spatial Variation in the Concentration of Labile Metals in the Overlying Water

Although there is no significant difference between labile metals in the surface and the bottom water, a statistically significant seasonality can be found in labile Zn and Pb in surface water, as well as labile Cd and Pb in bottom water (Table 4.3). However, no general seasonal variation pattern can be concluded from the results. Different metals show different variation pattern. Zn and Cd are higher in winter and spring, but Cu and Pb are higher in summer and autumn (Table 4.4). Similarly, no general pattern can be depicted from the variation of labile metals among sampling locations (Table 4.5). In short, there is no depictable trend in the variations of labile metal content along the river.

Table 4.3. Significance Level of ANOVA Test on Variation of Labile Metals between Seasons

Labile Metals	Water Layer	Significance Level of the Variation between Seasons
Zn	Surface	0.001
	Bottom	> 0.05
Cd	Surface	> 0.05
	Bottom	0.001
Pb	Surface	0.001
	Bottom	0.001
Cu	Surface	> 0.05
	Bottom	> 0.05

Table 4.4. Mean Labile Metal Concentrations (μg/l) in Four Seasons

Season	Zn (μg/l)		Cd (μg/l)		Pb (μg/l)		Cu (μg/l)	
	S	B	S	B	S	B	S	B
Spring	461.9	423.2	0.35	0.31	2.19	2.26	6.44	3.03
Summer	256.6	287.7	0.13	0.09	3.78	3.24	9.04	7.88
Autumn	267.0	322.9	0.31	0.03	5.51	5.28	5.99	8.42
Winter	387.1	308.9	0.45	0.16	3.14	2.72	2.72	2.51

*S =surface water
B =bottom water

Table 4.5. Mean Labile Metal Concentrations (μg/l) at Different Locations

Location	Zn (μg/l)		Cd (μg/l)		Pb (μg/l)		Cu (μg/l)	
	S	B	S	B	S	B	S	B
1	452.2	319.2	0.81	0.25	5.82	4.61	16.12	5.25
2	290.3	466.3	0.16	0.11	3.90	3.48	3.51	3.55
3	311.9	357.1	0.15	0.14	3.07	3.38	4.72	4.99
4	308.8	259.9	0.32	0.10	3.62	4.27	10.26	5.12
5	324.9	288.6	0.24	0.10	3.11	3.12	4.24	15.63
6	486.8	270.9	0.26	0.31	3.04	3.30	3.77	6.12
7	357.6	279.0	0.43	0.24	3.26	2.85	4.25	3.11
8	290.7	309.1	0.27	0.06	4.64	3.72	5.22	4.97
9	319.9	501.8	0.20	0.10	3.71	2.89	9.11	3.95
10	276.8	356.1	0.74	0.11	3.18	2.92	3.71	3.62
11	358.1	322.5	0.09	0.08	3.17	2.98	2.70	3.84
12	339.5	298.8	0.09	0.20	3.36	2.98	4.96	5.35

*S =surface water
B =bottom water

4.1.3 Percentage of Labile Fraction in Total Metals

In addition to the concentration of labile metals in the overlying water, it is also useful to know the share of labile metals in the total metals as it is indicative of the proportion of metals that is bioavailable. The diagrammatic comparison of total and labile metals are given in Figure 4.1 and Figure 4.2. The average labile fraction as percentage of the total metals is given in Table 4.6.

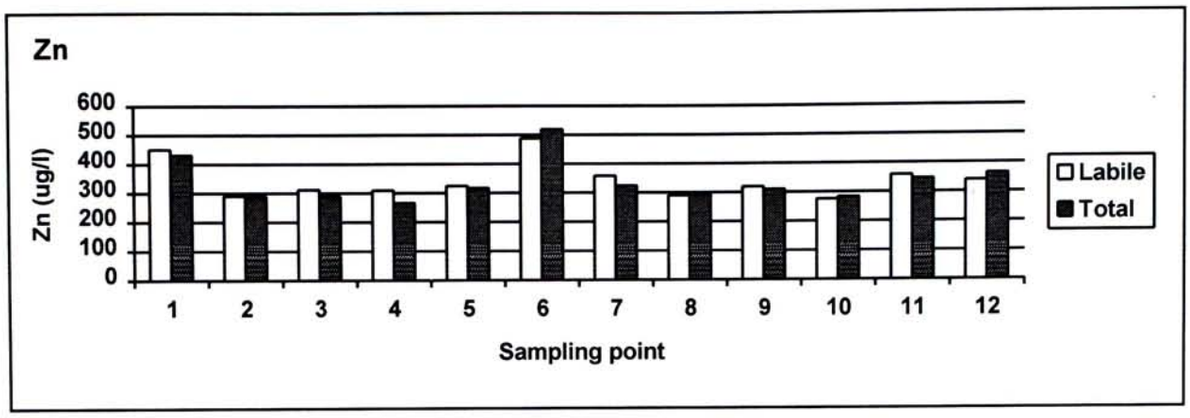
Table 4.6. Percentage of Total Metals in Labile Fraction

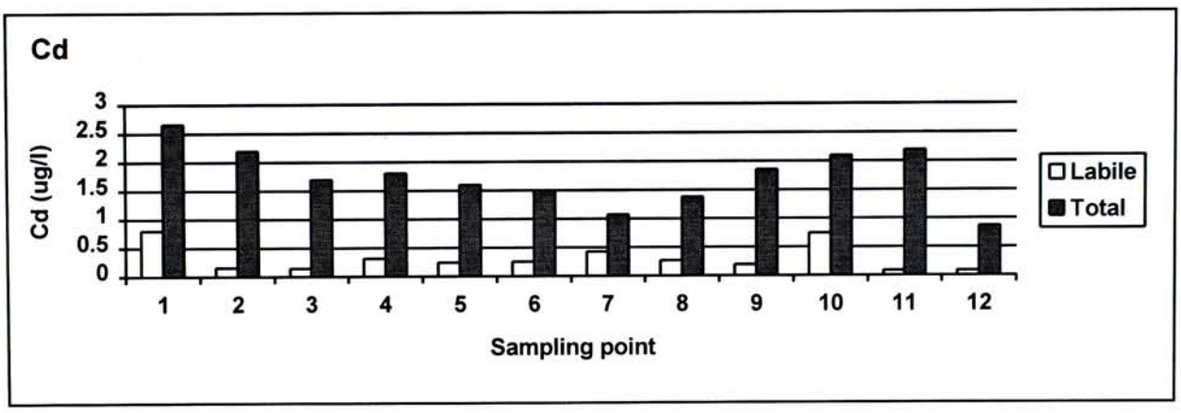
	% of Total Metals	
Labile Metals (μg/l)	**Surface Water**	**Bottom Water**
Zn	110	115
Cd	22	16
Pb	27	33
Cu	29	22

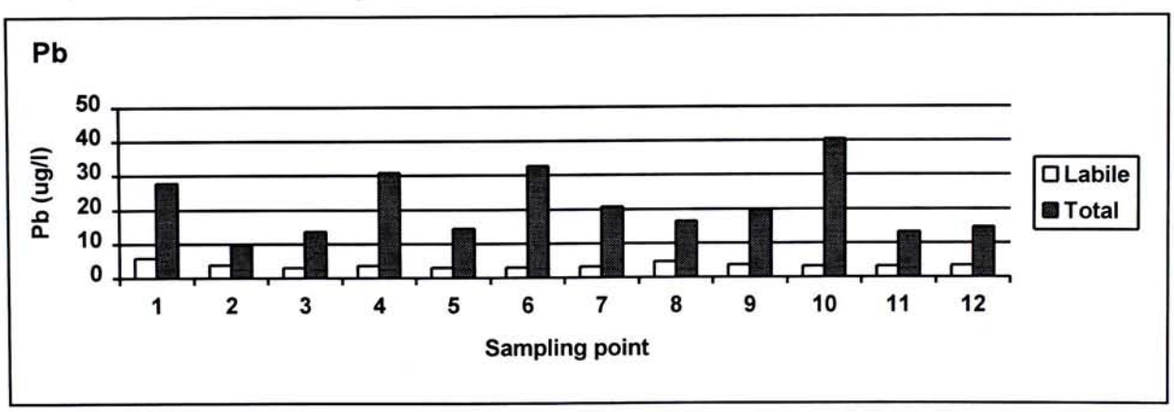
Labile Cd in overlying water accounts for about 20% of the total metals. Since the concentration of labile Cd is below 1 ppb, the actual amount of labile Cd that is available for biota is, indeed, very small. Labile Pb and Cu, on the other hand, account for about 30% of the total metal concentration. The labile fraction of Pb and Cu are small because they are probably partitioned, respectively, with chlorine and organic substances in seawater (Babukutty and Chacko, 1995; Jonasson, 1977). In summary, there are evidences to show that over 60% of the Cd, Cu, and Pb exist in the non-bioavailable form in the water column.

An unexpected phenomenon is observed in the data presented. The level of labile Zn is found to be greater than total Zn throughout the year except in spring. There is no apparent reason for this anomaly, except that it may be relevant to point out that different methods were used to measure labile and total Zn. The former was measured by anodic stripping voltammetric method (ASV) and the latter by absorption spectrophotometric method (AA). Different methods may have varying degree of analytical accuracy. Notwithstanding the anomaly, it can be said that a larger proportion of Zn in the water occurs in the labile form.

Figure 4.1. Comparison of Labile and Total Metals in the Surface Overlying Water at Different Locations







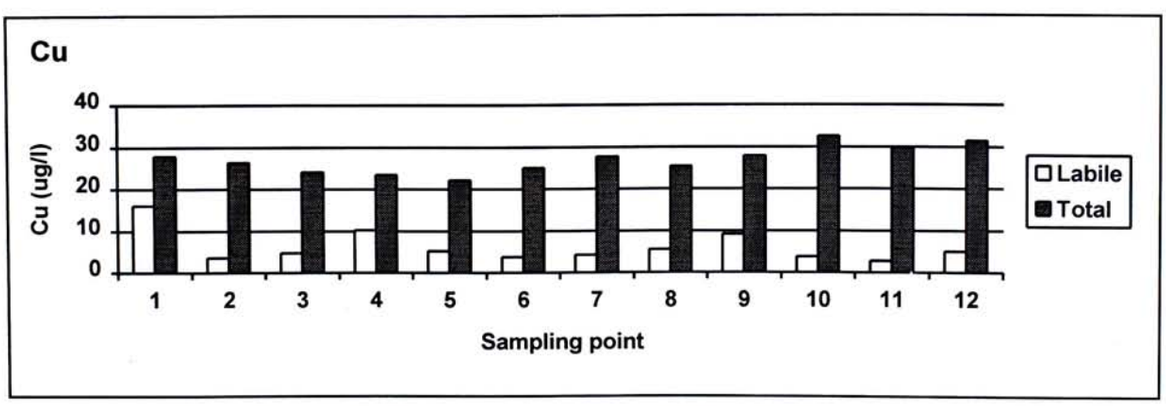
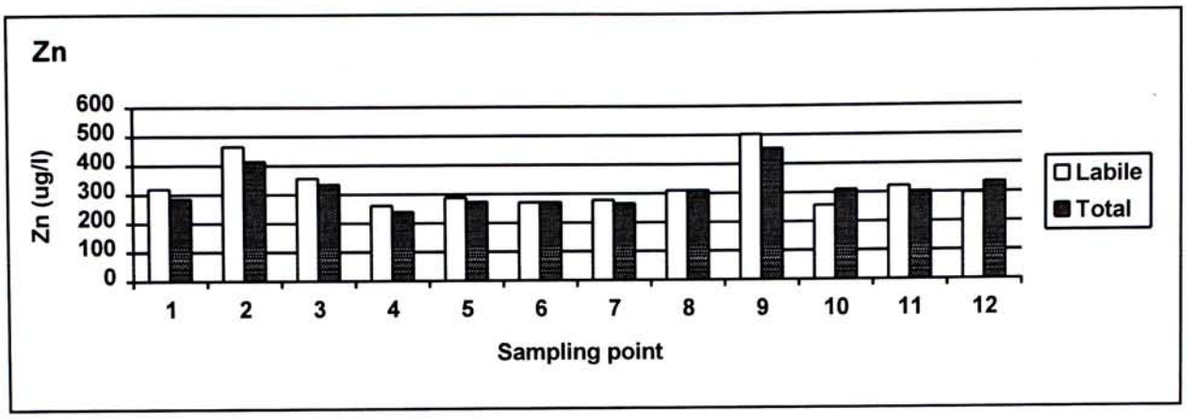
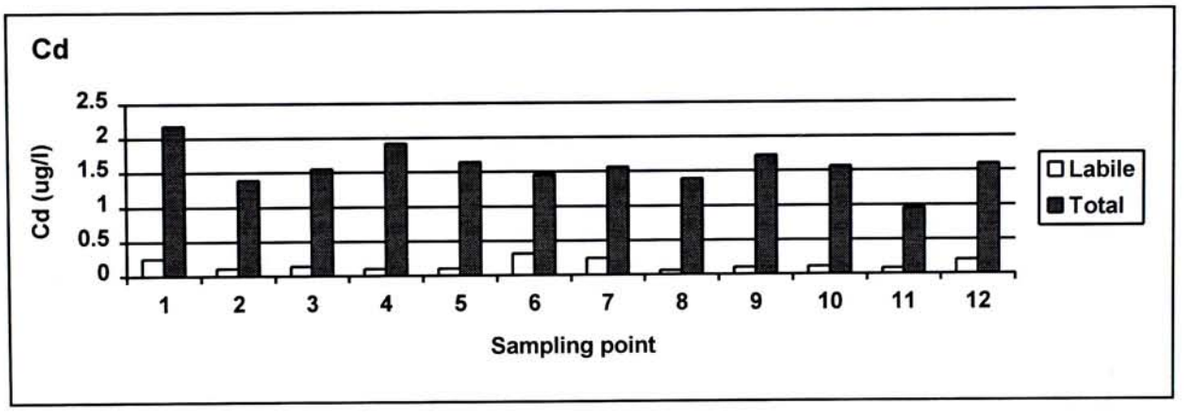
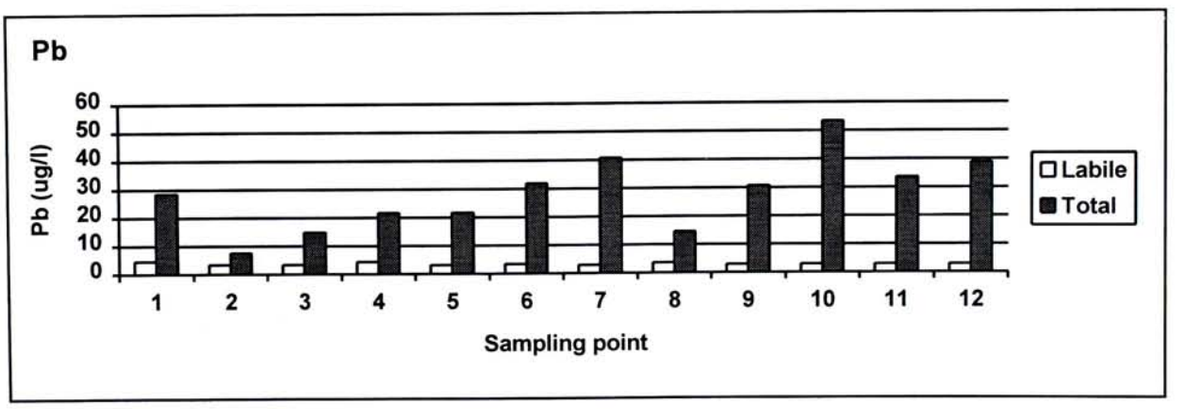
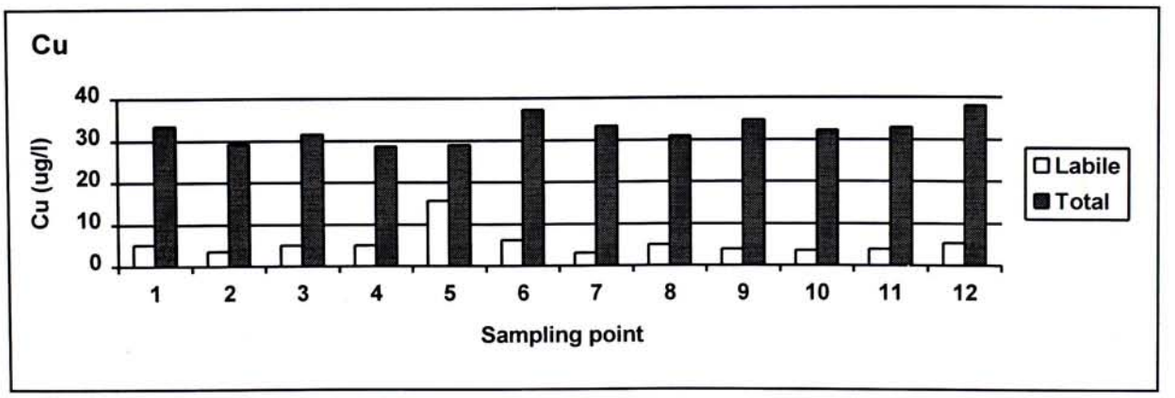


Figure 4.2. Comparison of Labile and Total Metals in the Bottom Overlying Water at Different Locations









In short, labile metals in the overlying water occur only in trace amount at the ppb range and no significant difference between the surface and bottom water can be observed. With the exception of Zn, only a small fraction of metals in the water occurs in the labile form. Therefore, the majority of the metals in the overlying water are not readily available to the aquatic life. Consequently, although concentrations of labile metals vary seasonally, with regard to their trace amount, their variation has little implication on the metal bioavailability.

4.2 SPECIATION OF METALS IN BOTTOM SEDIMENTS

Metals in the water column not only originate directly from human inputs, but also from the contaminated bottom sediments through remobilization which is especially outstanding in an estuary environment. Some previous studies carried out in coastal areas suggest that the estuary is a dynamic system conducive to the remobilization of metals. Forstner and Witmann (1979), for example, observed that "it is hardly possible to envisage a more abrupt change in natural systems than the one which takes place in the mixing zone between river and sea and it is therefore to be expected that the heavy metal loads will also be affected by these changes".

Estimation of metal remobilization under changing environmental conditions and the potential uptake by biota thus are the two major objectives of metal speciation study. The availability of trace metals to organisms may be influenced by

factors such as (1) physiological and ecological characteristics of the organisms, (2) changes of the chemical and physical characteristics of water and (3) the form of trace metal in solids. Since the first factor is outside the scope of this study, the discussion will only focus on the speciation of "metal loads" in the sediments and the "environmental changes" in the estuarine environment. Finally, the implication of such environmental changes on metal remobilization will be discussed.

4.2.1 Proportion of Various Metal Species in the Sediments

The speciations of metals in the sediments reflect a complex set of processes, such as adsorption, precipitation and coprecipitation. These processes regulate the partitioning of metals with various compartments such as dissolved inorganic and organic ligands and particulate matter. As a result, metals in the bottom sediments exist in a variety of physiochemical forms. These forms will largely determine the post-depositional mobility of the metals from sediments.

To determine the portion of various metal-binding phases, the sequential extraction method developed by Tessier and other (1979) was used. This method categorizes the metals into five phases: (1) ion-exchangeable (Phase I); (2) bonded to carbonates (Phase II); (3) bonded to Fe-Mn oxides (Phase III); (4) bonded to organic matters and sulfides (Phase IV); and (5) in residual form (Phase V).

At least two metal speciation work have been done on the sediments in Hong Kong (Hong, 1992; Kwok, 1993). Both of them have indicated that the phase of

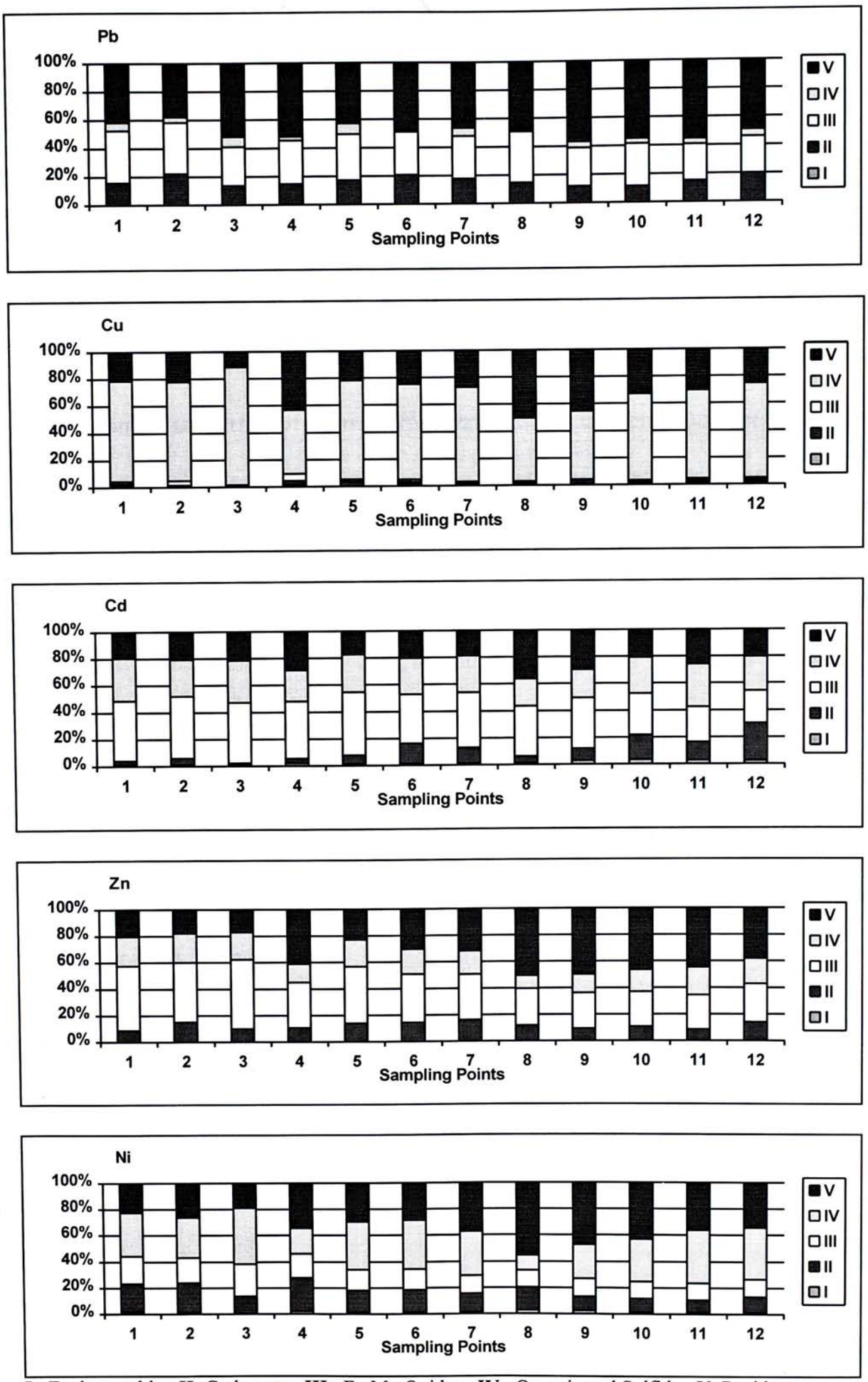
organic matters and sulfides is the most important, followed by the Fe-Mn phase. Results of this study (Table 4.7 and Figure 4.3) exhibit a pattern of metal speciation distribution similar to those studies conducted by Hong (1992) and Kwok (1993) in Victoria Harbour and Tsuen Wan, respectively.

Table 4.7. Speciation of Particulate Metals in the Sediments

	% of Total Metals				
Metal	**Exchangeable**	**Carbonate**	**Fe-Mn Oxide**	**Organic & Sulfide**	**Residual**
Pb	0.1	16.4	31.1	4.5	48.0
Cu	0.9	1.8	1.8	67.0	28.4
Cd	1.9	9.5	38.8	26.6	23.2
Zn	0.2	11.8	36.4	18.3	33.4
Ni	1.6	16.1	16.5	32.8	33.0

As mentioned above, the fourth phase, i.e. organic matters and sulfide, is the dominant metal-binding phase among the various phases. As much as 67% of Cu is associated with the organic matters and sulfides. For Ni, Cd, Zn and Pb, organic-sulfide phase accounts for 33%, 27%, 18%, and 4.5% respectively. Second to the phase of organic matters and sulfide is the phase of Fe-Mn oxides. The metals in residual form are less than half of total metals present in the sediments, suggesting that most metals are mainly derived from human inputs rather than from weathering of bedrock. It is also noteworthy to point out that only a small amount of metals is associated with the first two phases, namely ion-exchangeable and carbonate. Theoretically, metals existing in the ion-exchangeable form are most bioavailable to the aquatic life. The absence of these metal speciations suggests the metals do not pose significant hazard for the aquatic life under existing conditions.

Figure 4.3. Percentage of Different Speciation of Metals in the Sediments



I : Exchangeable **II**: Carbonate **III** : Fe-Mn Oxides **IV** : Organic and Sulfide **V**: Residue

To summarize, Phase IV (organic matters and sulfides) is the most important metal binding phase in the study area. There is also considerable amount of metals associated with Fe-Mn oxides in the sediments. About half of the total amount is in the residual form which is most difficult to be released from the bottom sediments. As for the metal speciation distribution in the study area, there is some potentials for metals to be released under the changes of environmental conditions. The extent to which these metals will be remobilized from the sediments depends on physiochemical properties of the overlying water and their fluctuation over time.

4.2.2 Variation of the Overlying Water Properties

The experimental data of Lu and Chen (1977) suggested that the remobilization of metals in bottom sediments was not controlled by the grain size of the sediments, but rather by the chemistry of the overlying water. Therefore, this section will describe the physio-chemical properties of the overlaying water in the study area. Then, attention will be given to the variation of the water properties throughout the year and its implications on metal remobilization. The physiochemical properties of the overlying water include pH, Eh, water temperature, dissolved oxygen, salinity and turbidity. The raw data of water quality of each season are given in Appendix E, and the spatial and seasonal means are listed in Tables 4.8 and 4.9.

4.2.2.1 Chemical Properties of the Water in the Study Area

The water properties at each sampling location are summarized in Table 4.8 and Figure 4.2. In the table, the coefficients of variation indicate the magnitude of variation of each water quality parameter. Among the parameters, Eh, turbidity, DO and salinity can be seen to exhibit the greatest variability over space. The variability of pH and temperature are relatively small.

Certain water quality parameters exhibit spatial trends along the river. Parameters which show an increasing trend from upstream to downstream area include pH, salinity and DO. The increasing pattern of pH and salinity mainly result from the mixing of sea and river water. Whilst the downstream increase in pH is evident, the magnitude of its variation, as indicated by the coefficient of variation, is small.

The parameter that shows a downstream decreasing trend is turbidity, which can be explained by the precipitation and flocculation of particulate materials in the river water as the river water mixes with sea water resulting in the settling of suspended solids (Forstner and Witmann, 1979).

Among all of the parameters, water temperature does not show any apparent variation pattern as revealed by the small coefficient of variation and narrow temperature range. Moreover, the difference of water temperature between surface and bottom water layers is greater in upstream than in downstream area due to an increasing degree of mixing of freshwater and seawater in the downstream area.

In contrast to water temperature, Eh of water is the most variable parameter. The Eh values of the first few upstream sampling locations are very different from that of the remaining locations. The contrasts of Eh between the surface and bottom water in the upstream locations are very large (Figure 4.4). It can be seen from the figure that the difference between the surface and bottom Eh is gradually reducing in the downstream direction and converges to 0 mv.

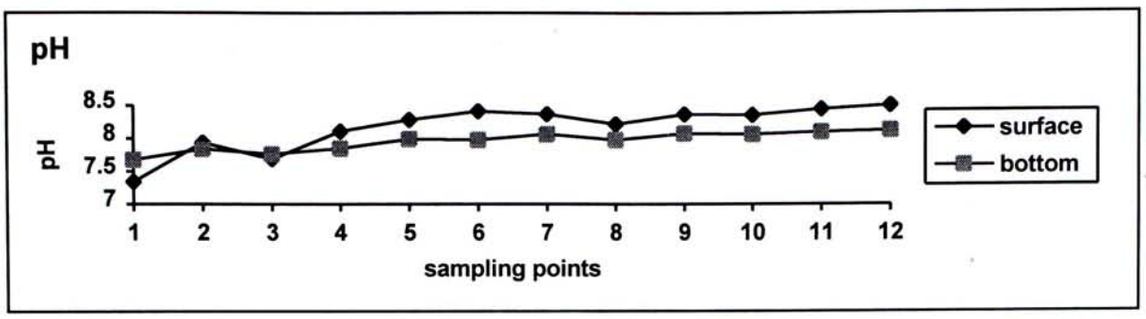
Table 4.8. Variation of Water Properties among Sampling Locations

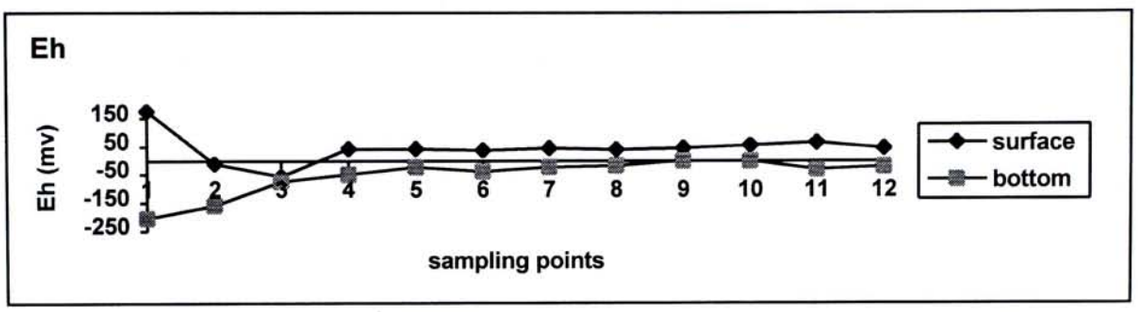
	pH		Eh(mv)		Temp(°C)		DO (mg/l)		Salinity (ppt)		Turbidity (mg/l)	
locations	S	B	S	B	S	B	S	B	S	B	S	B
1	7.34	7.67	175	-206	22.5	23.9	3.8	1.6	16.2	26.9	355	330
2	7.94	7.84	-10	-160	22.4	23.9	6.0	2.1	19.0	26.4	340	314
3	7.68	7.76	-56	-74	23.1	23.9	4.5	3.0	19.5	26.0	305	277
4	8.11	7.85	41	-48	22.6	24.2	5.9	3.4	21.1	26.3	368	275
5	8.28	7.99	41	-24	22.9	23.8	7.4	4.7	23.0	26.5	294	232
6	8.41	7.98	37	-39	23.3	23.8	7.5	3.7	23.8	30.3	232	219
7	8.37	8.06	43	-24	23.1	23.8	7.7	4.1	24.6	31.1	188	187
8	8.22	7.98	38	-19	23.4	23.7	6.1	3.7	24.0	29.8	270	122
9	8.37	8.08	45	2	23.7	23.6	8.1	4.7	25.2	30.8	143	125
10	8.36	8.07	54	2	23.5	23.7	8.4	4.2	26.0	31.7	139	130
11	8.45	8.10	63	-31	23.8	23.6	8.2	3.5	26.5	32.3	138	121
12	8.50	8.12	43	-20	23.9	23.7	8.7	2.3	26.4	31.2	130	109
mean	8.17	7.96	43	-53	23.2	23.8	6.9	3.4	22.9	29.1	242	203
range	7.34-8.50	7.67-8.12	-56-176	-206-2	22.4-23.9	23.6-24.2	3.8-8.7	1.6-4.7	16.2-26.5	26.0-32.3	130-368	109-330
C.V.	0.04	0.02	1.23	-1.21	0.02	0.01	0.23	0.29	0.14	0.08	0.38	0.40

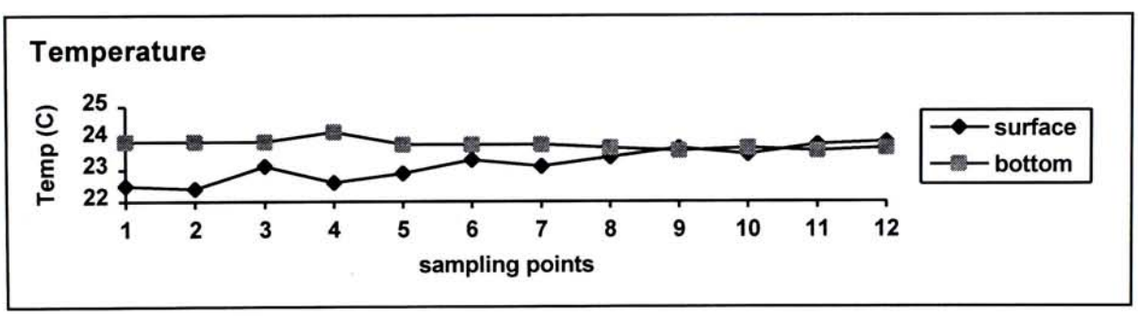
*C.V. = Coefficient of variation

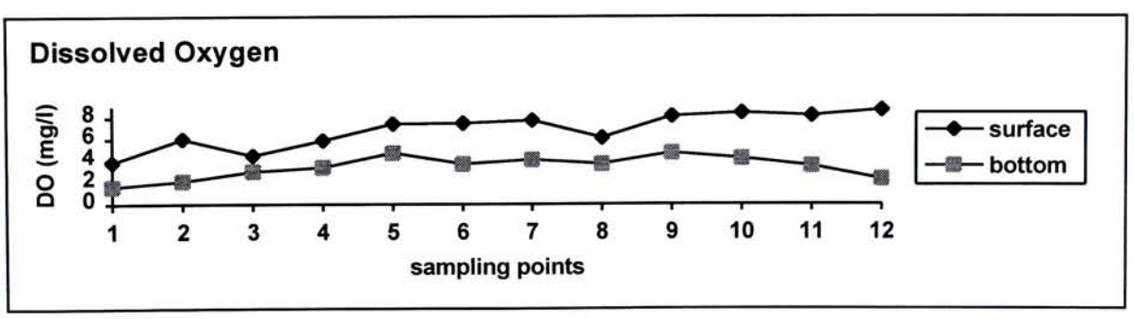
Besides the general description of the water chemical properties, the variation of these water properties over time will also be investigated. This aspect merits attention because the temporal variation in the chemistry of overlying water can initiate metal remobilization.

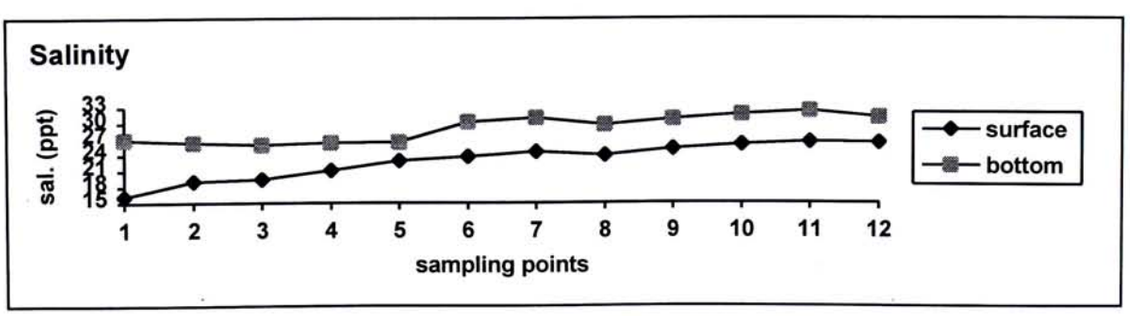
Figure 4.4. Variation of Water Properties among Sampling Locations

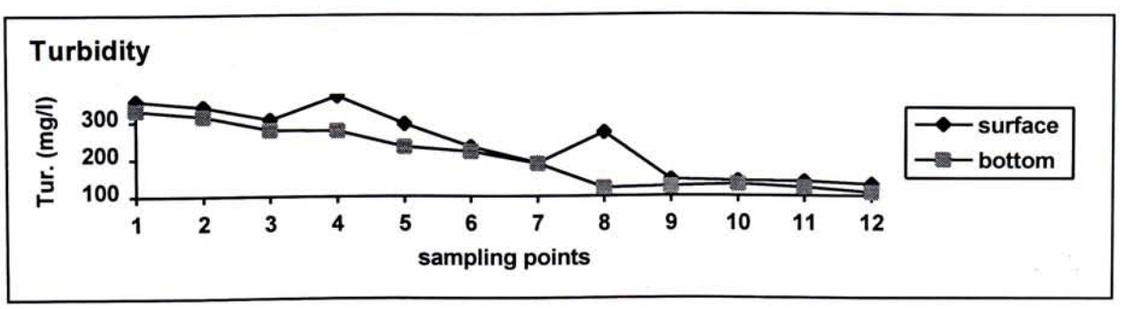












4.2.2.2 Seasonal Variation of Water Properties

The seasonal mean and range of the water properties are listed in Table 4.9 and portrayed in Figure 4.5 is the variation trend of water quality in different seasons. According to the results, each parameter seems to have its own seasonal variation pattern and there is no general trend that can be applied to all parameters. Even for the same parameter, the pattern of variation for the surface water is different from that of the bottom water.

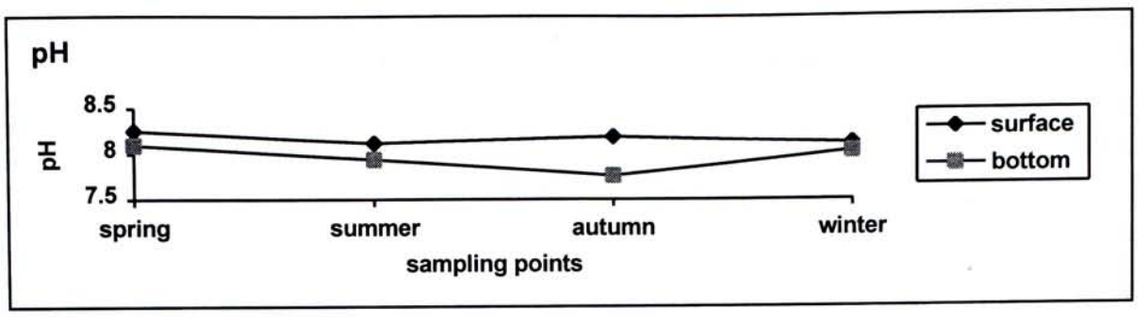
The magnitude of changes of different parameters, as shown by their coefficients of variation (Table 4.9), is also different. Generally speaking, Eh, temperature, DO, salinity and turbidity of water are more variable in different seasons, while pH exhibits the smallest variability.

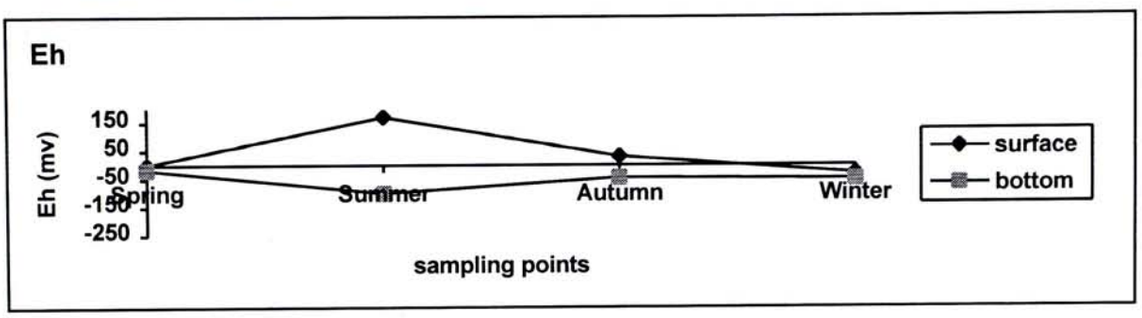
Table 4.9. Seasonal Variation of Water Properties

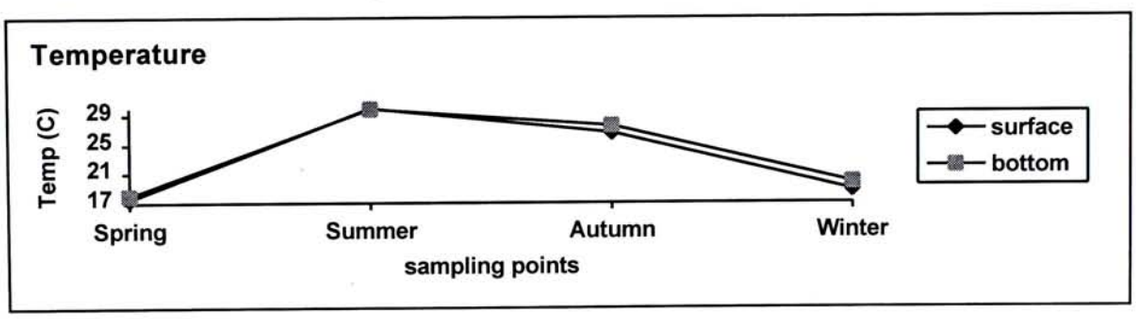
	pH		Eh (mv)		Temp (°C)		DO (mg/l)		Salinity (ppt)		Turbidity (mg/l)	
Season	**S**	**B**	**S**	**B**	**S**	**B**	**S**	**B**	**S**	**B**	**S**	**B**
Spring	8.25	8.09	1	-17	17.5	18.0	7.9	6.3	27.7	30.6	287	256
Summer	8.12	7.94	171	-101	30.0	29.9	7.4	4.6	28.3	31.5	212	235
Autumn	8.19	7.76	29	-46	26.6	27.6	9.0	1.3	9.6	24.7	192	166
Winter	8.12	8.03	-30	-49	18.7	19.8	3.1	1.4	26.0	29.5	274	156
mean	8.17	7.96	43	-53	23.2	23.8	6.9	3.4	22.9	29.1	242	203
range	8.12-8.25	7.76-8.09	-30-171	-17--101	17.5-30.0	18.0-29.9	7.4-9.0	1.3-6.3	9.6-28.3	24.7-31.5	192-287	156-256
C.V.	0.01	0.02	2.08	-0.05	0.26	0.24	0.38	0.72	0.39	0.10	0.19	0.24

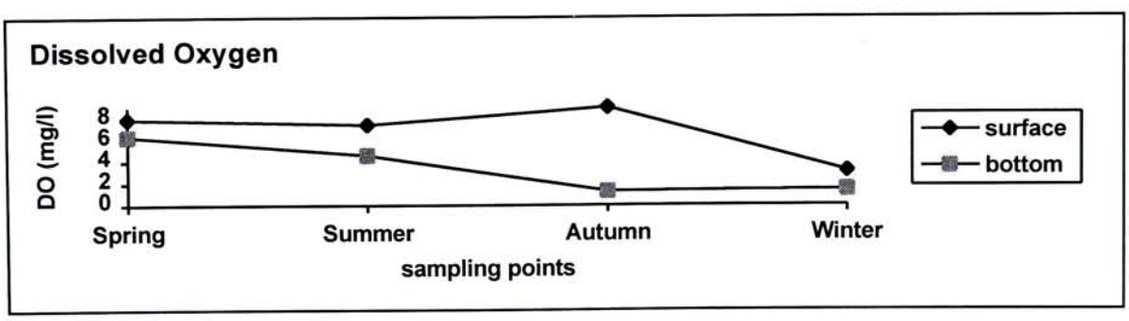
* C.V. = Coefficient of variation

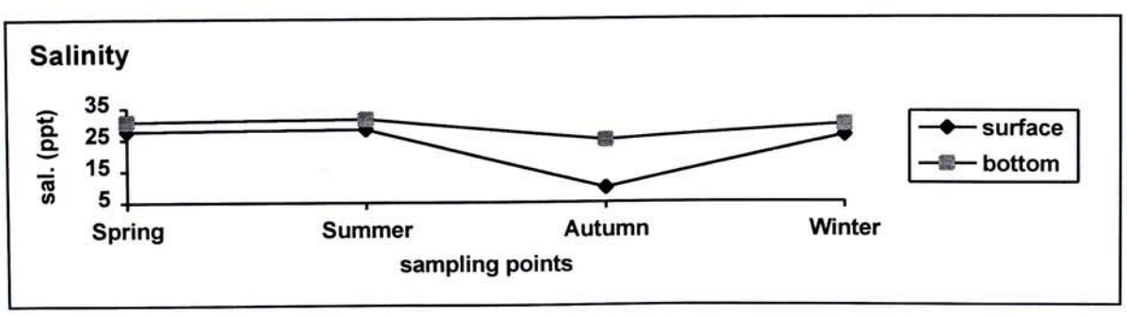
Figure 4.5. Variation of Water Properties among Seasons

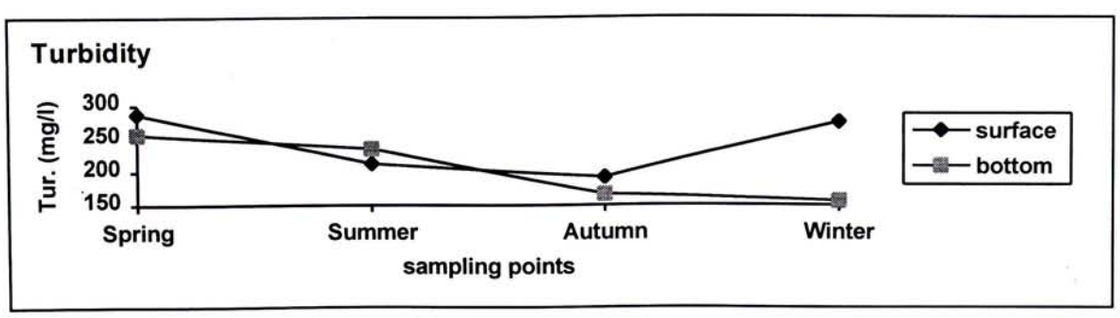












Despite the fact that Eh exhibits large variation in different seasons, it is not necessarily followed by remobilization of the metal from the bottom sediments. It can be seen that, for most of the time, in spite of the variations, the surface water remains in the oxic state (above 0 mv) and the bottom water in the transitional state between the oxic and the anoxic stage (-200 mv) (Rump and Krist, 1992).

As previously said, pH exhibits the smallest seasonal variation among all parameters. It is lower in summer and autumn and higher in winter and spring, but the fluctuations are confined to the range of 7.76 to 8.25.

4.2.2.3 Stratification of the Water Column

According to the monitoring results of EPD, stratification of the overlying water is a common phenomenon in the Tolo Harbour caused by the interaction of intense solar heating of the surface water and the intrusion of colder tidal current at the bottom. Stratification is relevant to this study because it has bearing on the release of metals from the bottom sediments and the subsequent redistribution of released metals in the water column.

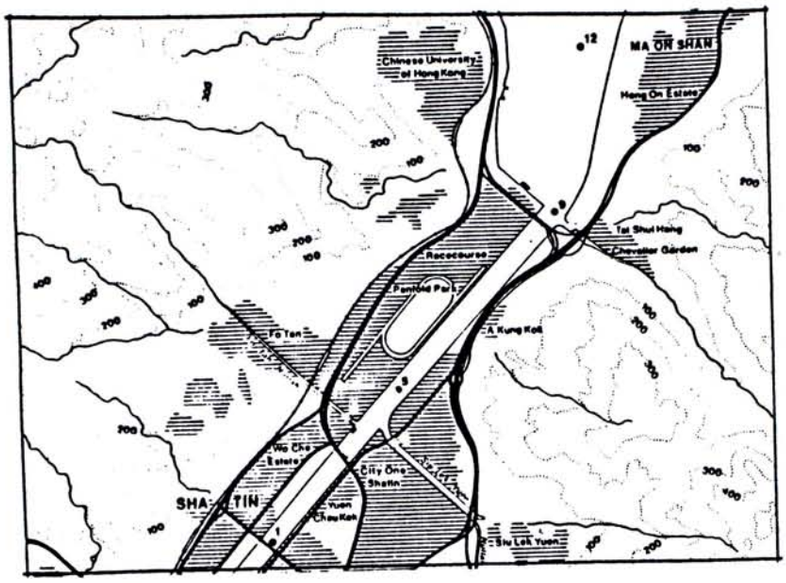
Stratification refers to the sudden change in water quality at a certain point along a vertical profile. When it occurs, it may impede the mixing of surface and bottom waters. In many cases, stratification can occur as a result of temperature change and the existence of different density layers. The former is climate induced and the latter brought about by the intrusion of a water body with a different salinity.

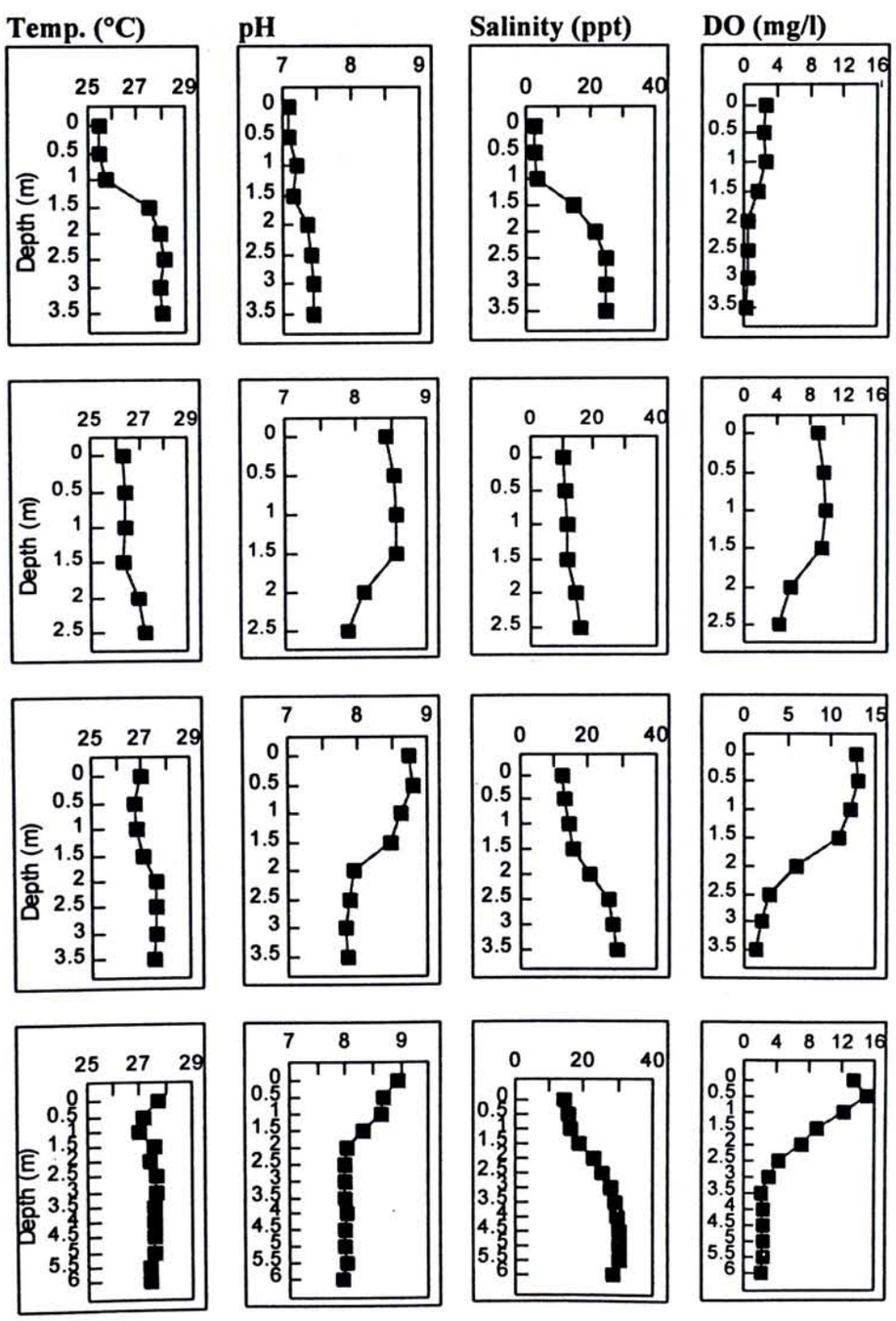
If mixing of surface and bottom waters is impeded, the anoxic condition close to the sea bottom will be reinforced, hence depressing the DO close to the sediment-water interface to very low levels. In order to ascertain the existence of stratification in the study area, the water quality was profiled at 0.5m interval in the summer, autumn and winter sampling trips. Because of the lack of profiling equipment, this was not measured in the first (spring) trip. The results for DO, salinity, temperature and pH are tabulated in Appendices O, P, Q and R respectively.

The data gathered does not seem to suggest the existence of stratification throughout the whole year. In general, it is very weak in summer and winter but much more pronounced in autumn. To illustrate this point, the vertical profile of pH, temperature, salinity and DO for the autumn season at some selected sampling locations are portrayed in Figure 4.6. Abrupt changes in all water parameters can be seen at about 1-2m from the surface. However, the magnitude of change is different for different parameters, as are for the differences of same parameter among upstream and downstream areas.

Among the parameters, the magnitude of variation of DO and salinity is larger than that of pH and temperature (Figure 4.6). This is not unexpected. Seawater is a well-buffered system and change in pH only occurs after the influx of large volume of storm water in the summer season. Likewise, the seawater body is a huge store of heat energy and it responds rather slowly to air temperature changes. The maximum difference of temperature between surface and bottom water is only 2°C.

Figure 4.6. Vertical Water Profile in Autumn at Some Selected Locations





Indeed, it can be found that the bottom water is warmer than the surface water. Such unstable thermal structure may lead to an overturning of water column (i.e., the warmer surface water moves upward to the surface layer and, at the same time, the cooler surface water will sink to the bottom).

On the other hand, the significant difference in surface and bottom salinity is caused by the intrusion of seawater, which is higher in density, into the channel. Because of the density difference, the intruding water moves close to the seafloor, whilst the freshwater runoff, having a lower density, tends to "float" above the seawater as a tongue which has lower salinity and pH. The much depressed DO level close to the sea bottom is largely due to the huge oxygen demand at the sea floor and the impediment of oxygen replenishment due to the existence of the water strata.

Stratification does not occur in the same intensity along the length of the river channel, it is more prominent in the upstream area. From the data collected (Fig. 4.4), it can be seen that the vertical change in temperature and salinity is most abrupt at location 1. The abrupt break in the vertical profile of salinity and temperature in the upstream (location 1) indicates a large tongue of inflowing freshwater lying above the seawater. This was most pronounce in autumn of 1995 which coincided with several episodes of heavy rain. This inflowing freshwater also dilutes the seawater, hence reducing its pH.

On the other hand, the change in the DO concentration is most abrupt in the inner harbour area, i.e. location 12. This difference in DO between the surface and bottom layer is due to the different rates of oxygen consumption and replenishment. At the surface, oxygen is replenished by photosynthesis and reaeration at the air-sea interface. At the bottom, oxygen is depleted by microbial decomposition of the rich organic matters in the bottom sediments. Stratification impedes the diffusion of oxygen from the upper to the lower water layer, resulting in an abrupt change of DO concentration at about 1m from the surface. Therefore, the bottom water is constantly kept in an anoxic environment.

4.2.3 Implication of the Changes of Water Quality on Metal Remobilization

Since metals in the bottom sediments are mostly bound to organic matters, sulfides and Fe-Mn oxides rather than to minerals in the residual form, they may be easily remobilized as a result of environmental changes at the water-sediment interface. Remobilization was mainly caused by the chemical changes in waters, such as changes in the Eh conditions, lowering of pH and elevated water salinity (Forstner and Witmann, 1979). Therefore, this thesis will further examine whether the water quality changes, as described in former section, may induce metal remobilization. The impact of stratification on metal remobilization will also be looked at.

Among various water parameters that may affect metal remobilization, Lu and Chen (1977) considered Eh and pH as the most important. Theoretically, the lowering of pH will lead to the dissolution of carbonates and hydroxides, and may also enhance the desorption of metal cations due to competition with hydrogen ions (Forstner and Witmann, 1979). This postulation has been confirmed by other studies. For example, Gambell and others (1980) demonstrated that changes in pH would result in changes in the chemical availability of Pb, Zn and Hg of the sediment-water system. The work of Adams and Sander (1984) also indicated that the threshold pH for metal release from sludge was 5.8 for Zn, 6.3 for Ni and 4.5 for Cu. The pH of the river and harbour water in the study area is much higher than the above values, ranging from 7.76 to 8.25 for most of the time. In other words, the overlying water is not acidic enough to remobilize metals from the bottom sediments.

The temporal variation of the Eh values of the overlying water in the study area has little impact on metal remobilization. Since the bottom sediments are in contact with bottom water, so the focus would be placed on the bottom water. As previously mentioned, the bottom water is in a state close to the anoxic condition through out the study period (Table 4.9). Under such reducing environments, Fe and Mn could be released in significant quantities due to the dissolution of Fe-Mn hydroxides. But Fe and Mn are not investigated in the study, so the increase of their concentrations in the overlying water is not known.

On the other hand, under the reducing environment, Cd, Cu, Ni, Pb and Zn are immobilized in the sediments due to the formation of metal sulfides or bound to organic matters (Lu and Chen, 1977). If the above assumption is correct, then, one might expect that there is only very little amount of metals released from the sediments and hence little variation of metal concentrations in the overlying water. However, in reality, there is significant variation of labile Zn, Cd and Pb in either surface or bottom water among different seasons. The concentration of labile metals in the overlying water is thus apparently not simply under the influence of metal remobilization. Several other factors may contribute to such phenomenon, such as biological uptake and immobilization process. This study cannot ascertain which factors are involved.

Water salinity is another determinant of metal remobilization. An increase in salinity is known to enhance metal release as the increased alkali and alkaline earth cations can compete for the sorption sites on the solid particles thus displacing the metal ions from the sediments (Forstner and Witmann, 1979). Most of the previous studies focused on the effect of increased salinity on metal remobilization from suspended solids. For example, the study of Patchineelam and Calmano, cited by Forstner and Witmann (1979), was on the release of metals from polluted suspended sediments introduced into a seawater environment. They reported that about 10% of Zn, Co and Cr were remobilized. It should be noted that unlike most previous studies, the bottom sediments in the study area are not subject to an increase in salinity, but rather to a reduction in salinity caused by the influx of freshwater in the rainy seasons. Therefore, no significant metal remobilization is expected.

As mentioned above, the amount of metal remobilized from the sediments is very small, so only trivial amount of metals can move upward either by diffusion or the overturning of water column.

To summarize, most of the metals in the sediments are in the non-residual form and are thus subject to the influence of the physiochemical properties of the overlying water. Whilst the properties of the overlying water may vary over time, the lowering of pH and increase in water salinity that was experienced in the study period is unlikely to cause any metal remobilization of a significant scale. Moreover, under a reducing environment, although some Fe and Mn may be released, Cd, Cu, Pb and Zn are immobilized in the sediments by binding to organic matters and sulfides. Therefore, the actual amount of metals introduced into the overlying water is small.

CHAPTER 5

VARIATION OF AVS AND ITS ROLE IN METAL TOXICITY MEDIATION

This chapter is going to determine the variation of AVS in the spatial, temporal and vertical dimensions and to assess its effects on metal bioavailability. As mentioned in chapter 1, most of the Hong Kong's coastal marine sediments are in an anoxic condition. In this anoxic environment, Acid Volatile Sulfide (AVS) is the dominant mediator of metal toxicity. The importance of AVS has received lots of attention in recent years because of its ability to mediate metal bioavailability and hence toxicity in two ways. Firstly, metals can precipitate directly with AVS to reduce its bioavailability. Secondly, the more toxic metals, which have a higher affinity for AVS, can displace the less toxic metals to form more insoluble metal sulfides (Howard and Evans, 1993). This displacement process can reduce the overall metal toxicity. However, there are certain biogeochemical processes in the marine environment which can produce substantial variations in AVS concentration. Therefore, the metal bioavailability and toxicity of bottom sediments at various sampling locations may be different from one another.

In assessing the role of AVS, focus will be placed on the "Simultaneously Extracted Metals" (SEM)/AVS ratio and the fraction of labile metals in the

sediment-water matrix. Furthermore, the role of dissolved sulfide in pore water will also be discussed.

5.1 VARIATION OF AVS IN THE STUDY AREA

AVS in the bottom sediments is not constant through space and time. It exhibits vertical, temporal and spatial variations which make the evaluation of potential metal toxicity difficult. This section will specifically evaluate the variability of AVS in the study area.

5.1.1 Spatial Variation of AVS

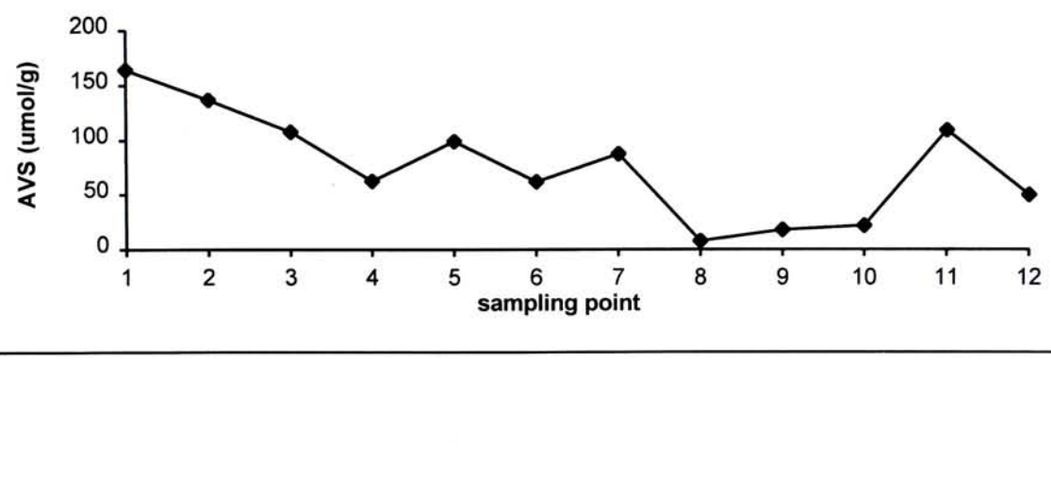
Table 5.1 shows the mean and range of AVS in the bottom sediments. AVS concentration varies considerably among sampling locations. Higher AVS concentrations are recorded at locations 1, 2 and 3 in the upstream area and location 11 in the inner Tolo Harbour, while lower values are found at locations 8, 9 and 10 which are located near the estuary (Figure 5.1).

Table 5.1. Variation of AVS (μmol/g) among Sampling Locations and Seasons

Variation	Mean	Range
sampling locations	79.2	7.1 - 164.1
seasons	76.8	51.7 - 106.8

As the concentration of AVS is controlled by the supply of sulfate which is a major component of seawater, one would expect AVS to be significant only in marine sediments. However, other studies indicated that AVS in freshwater system could be as high as in marine systems (Lin, 1990). As Shing Mun River is a tidal river, the channel is swept by tidal currents and the supply of sulfate is not a problem in the entire length of the channel. In other words, sulfate supply is not a limiting factor in AVS formation.

Figure 5.1. Spatial Variation of AVS in the Study Area



The daily swash and backswash of the tide also bring sediments and organic matters up and down the channel. Since they are also the controlling factors for AVS formation, the distribution pattern of AVS in the tidal river is most probably different from the one in freshwater lake. To ascertain the factors governing the variation of AVS, the correlation among different sediment properties is listed in Table 5.2. Total carbon (TC), grain size, Eh and pH of the sediments show strong correlation with AVS contents.

Total carbon is one of the primary controlling factors of AVS formation. In the sulfate reduction processes, the bacteria require organic material as an energy source. Therefore, the rate of sulfate reduction greatly depends on the availability of organic carbon (Berner, 1970), while its concentration is inversely related to the sediment grain size. As a result, the upstream sampling locations which are rich in clay usually contain greater amount of organic matters and AVS, while the coarser sediments near the estuary contain less organic matters and AVS (Figure 5.2).

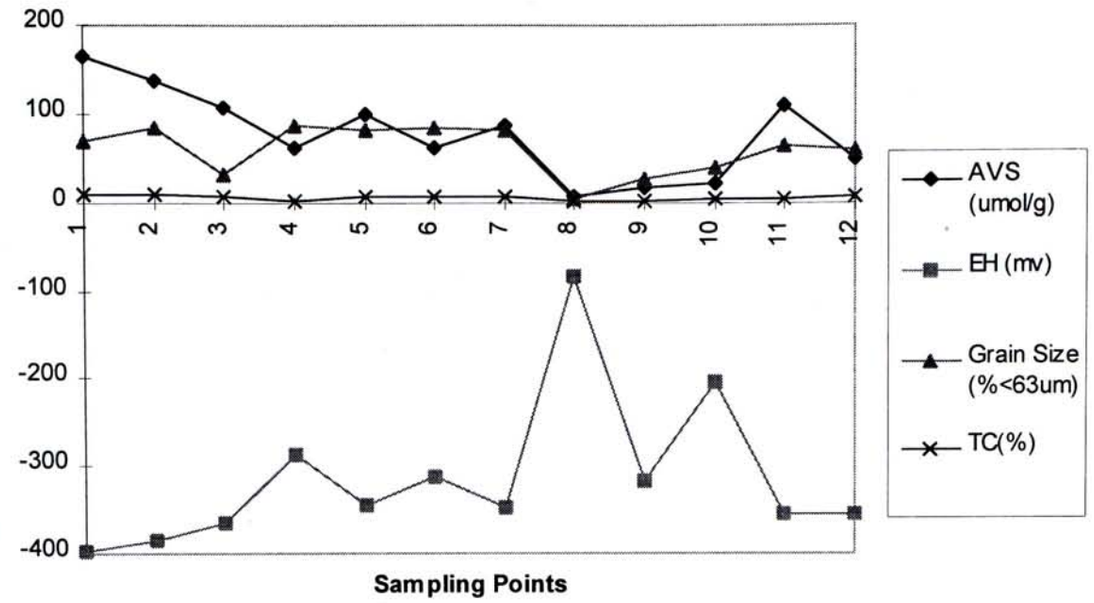
Table 5.2. Correlation Matrix of Sediment Properties

	pH	Eh	Temp.	AVS	TC	SEM	SEM/AVS Ratio	Grain Size
pH	1							
Eh	0.09	1						
Temp.	0.26	-0.22	1					
AVS	-0.48*	-0.57*	0.01	1				
TC	-0.39*	-0.21	-0.25	0.53*	1			
SEM	-0.53*	-0.44*	-0.12	0.75*	0.54*	1		
SEM/AVS	-0.01	0.50*	-0.09	-0.38*	-0.22	-0.22	1	
Grain Size	-0.04	-0.50*	-0.04	0.53*	0.42*	0.39*	-0.36*	1

* Significance Level of the Correlation is < 0.05

Grain size is not only the determinant of organic carbon content (Lin, 1990), but also to the Eh (redox potential) of the sediments (Table 5.2). Sandy sediments that have large porosity are usually in an oxic environment. In an oxic environment, in which Eh is positive, oxidation reduces the AVS concentration. Therefore, the more oxic is the environment, the lower is the AVS concentration. For this reason, the anoxic condition of upstream sediments provides a favourable environment for AVS formation and contributes to higher AVS concentrations (Figure 5.2).

Figure 5.2. Relation between AVS, Eh, Total Carbon and Grain Size

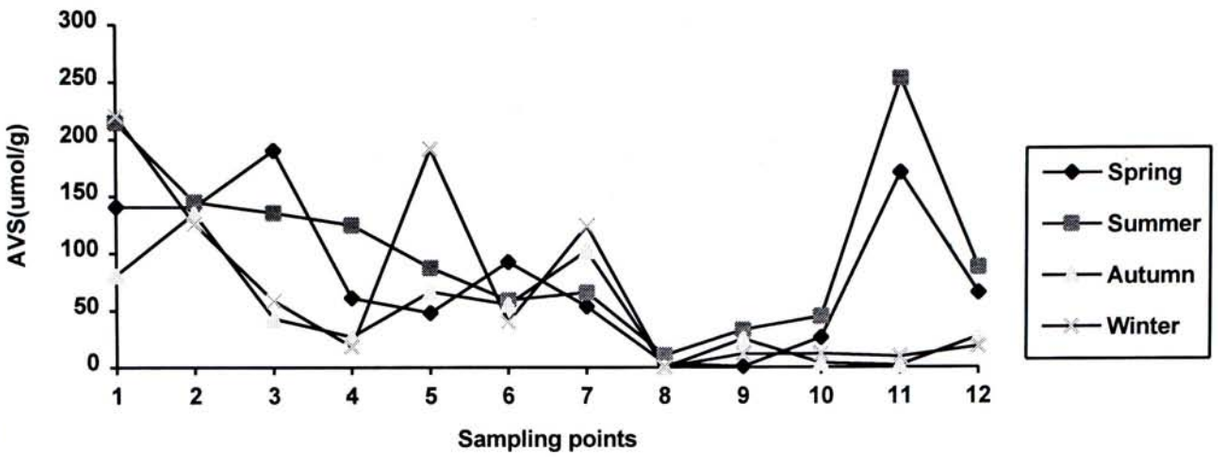


The relationship between pH and AVS concentration in this study seems to be contradictory to the findings of previous studies. Jorgensen (1977) indicated that a low pH environment favoured pyrite formation in Denmark coastal sediments, while Doyle (1968) suggested an increase of iron sulfide solubility when pH was reduced. All these findings draw the same conclusion that the decrease in pH value will reduce the amount of AVS. However, pH and AVS are negatively correlated in this study, which means that a decrease of pH usually associates with an increase of AVS. The reason for this negative correlation is not clear.

5.1.2 Seasonal Variation of AVS

According to Figure 5.3, it is apparent that AVS not only varies from location to location, but also from season to season.

Figure 5.3. AVS in Sediments at Different Sampling Locations in Four Seasons



The average concentration of AVS is in the order of summer > spring > winter > autumn (Figure 5.4). Regarding the seasonal variation pattern of AVS at individual locations (Figure 5.5), there is a similar pattern among them, i.e. AVS increases from spring to summer and drops to low in autumn. In the present study, the variation pattern is mainly controlled by two factors: (1) increase of water temperature and (2) reduction of organic matters in the bottom sediments. This is in agreement with what Howard (1992), Leonard and other (1993) and Lin (1990) reported.

Figure 5.4. Seasonal Variation of AVS in the Study Area

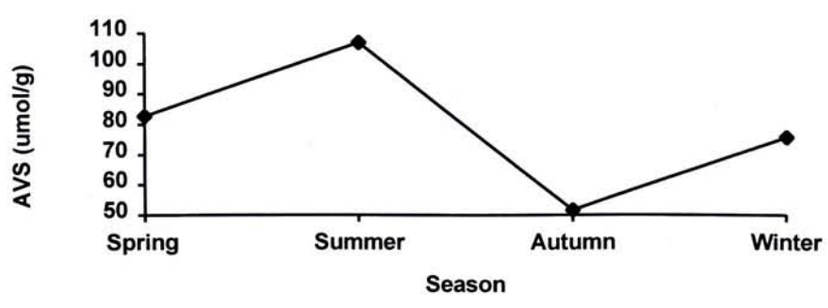
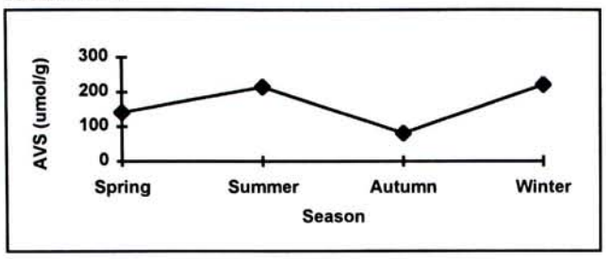
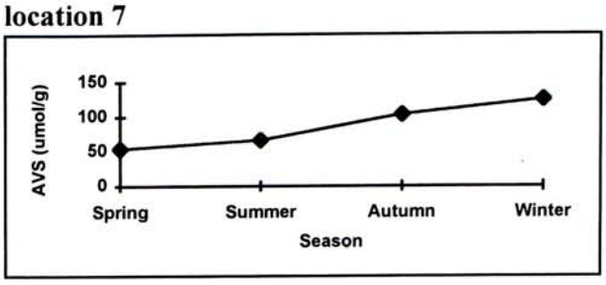


Figure 5.5. Seasonal Variation of AVS at Each Sampling Locations

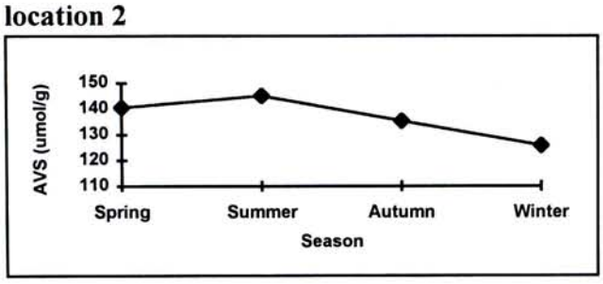
location 1



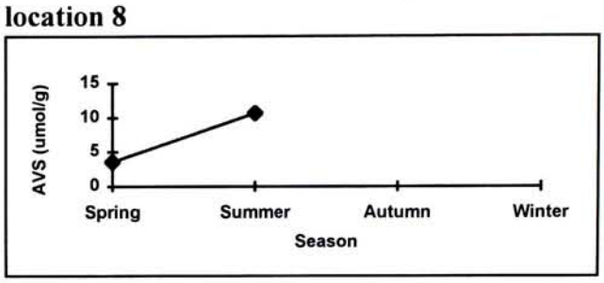
location 7



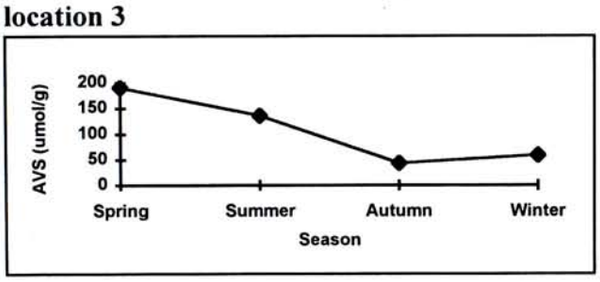
location 2



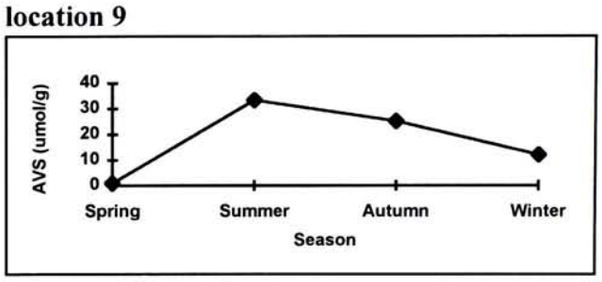
location 8



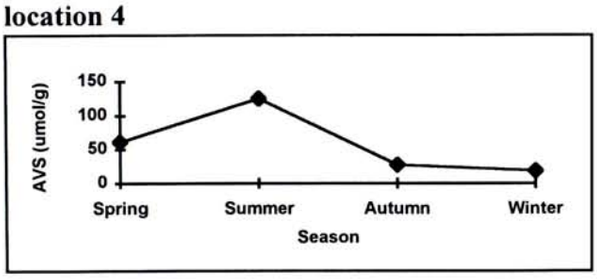
location 3



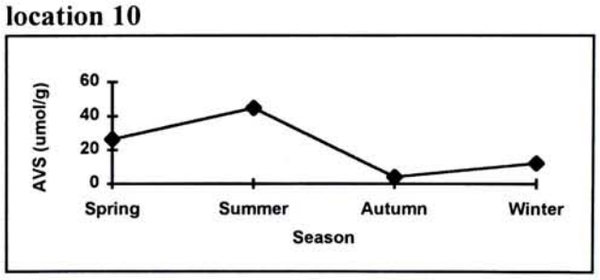
location 9



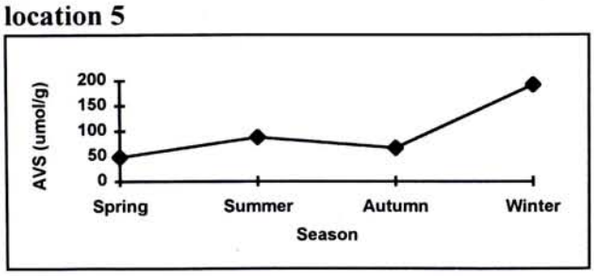
location 4



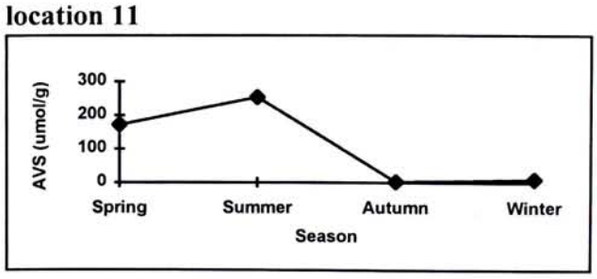
location 10



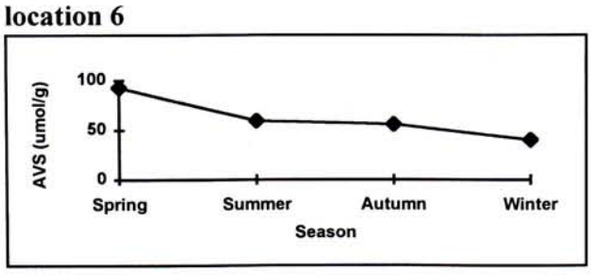
location 5



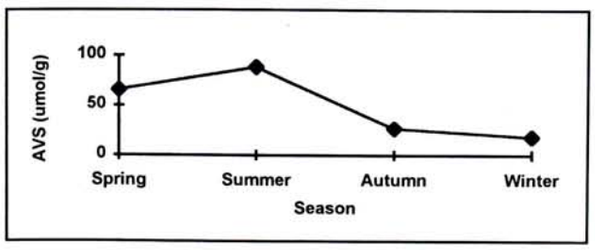
location 11



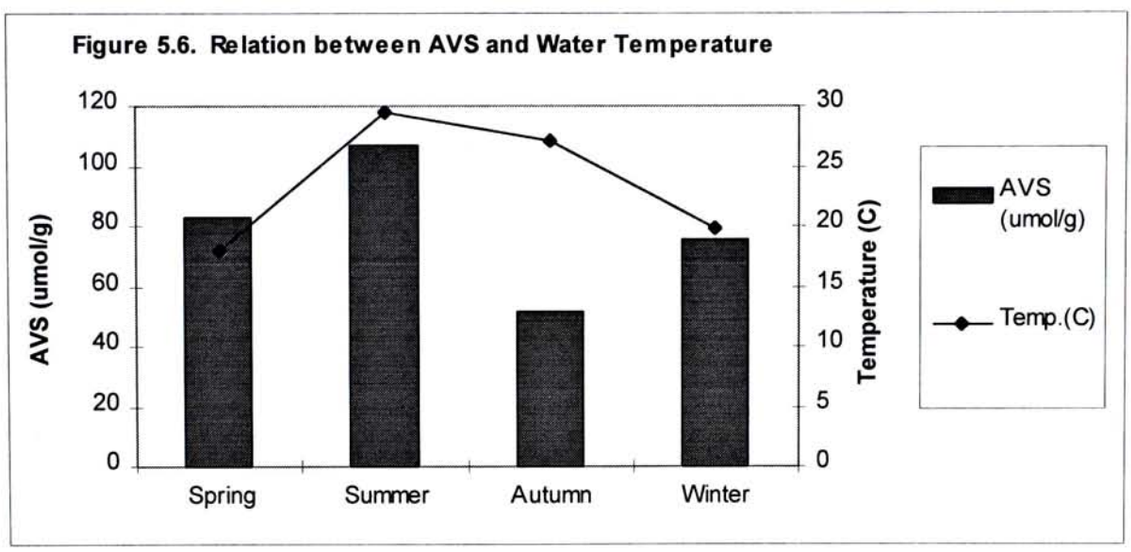
location 6



location 12



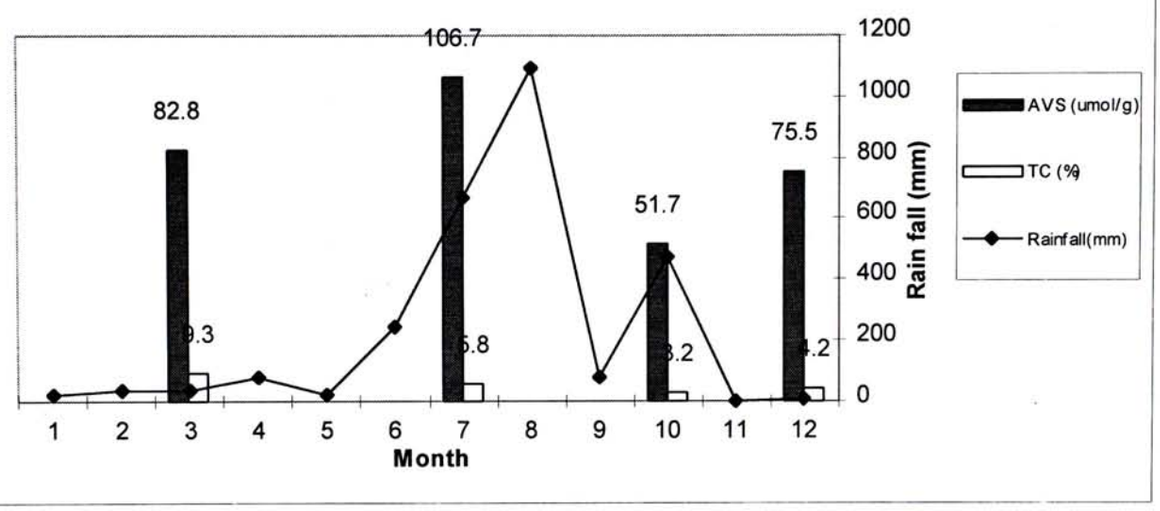
The increase in water temperature lead to an increase in AVS concentration from spring to summer. This increase of water temperature enhances the sulfate reduction process and consequently results in higher AVS concentration in summer (Figure 5.6).



Regarding the decrease of AVS concentration in autumn, the loss of organic matters in the bottom sediments is probably the major reason. According to the results (Figure 5.7), total carbon (TC) is at the maximum in spring and decreases in summer and autumn probably as a result of the heavy summer rainfall. In 1995, the greatest amount of rainfall was recorded in July, August and October (Figure 5.7). The storm in late summer and early autumn washed away the organic-rich sediments and at the same time brought down a lot of freshly weathered materials covering the seabottom. Since the amount of fresh organic matters available for anaerobic decomposition is also a controlling factor of AVS formation (Jorgensen, 1977),

newly deposited sediments do not provide sufficient organic matters to sustain the sulfate reducing bacteria. Consequently, a decrease in AVS concentration in autumn is observed.

Figure 5.7. Relation between AVS, Total Carbon and Rainfall



5.1.3 Vertical Variation of AVS

The concentration of AVS varies with depth brought about by the variability of iron, organic matters, sulfate and other properties in the sediments. The practice of homogenizing the sediment samples before chemical analysis may obscure such vertical variations. An understanding of the vertical variation of AVS thus is important in the assessment of AVS as a mediator of metal bioavailability and toxicity. To obtain information on the vertical profile of AVS concentration, sediment cores were collected at the twelve sampling locations in the autumn sampling trip.

Table 5.3. Characteristics of Sediment Cores

Location	Layer (cm)	AVS (μmol/g)	pH	Eh (mv)	Temp. (°C)	Sediment Colour*	Grain Size (brief description)
1	0-5	152.0	7.67	-378	19.6	Gley2.5 N2.5	siltly clay
	5-9	185.0	7.32	-357	19.4	Gley2.5 N2.5	siltly clay
2	0-6	101.9	7.76	-332	21.3	Gley2.5 N2.5	clayey silt
	6-16	48.9	7.89	-382	21.4	2.5Y. 2.5/1	clayly silt
	16-22	107.9	7.61	-375	21.3	Gley2.5 N2.5	clayly silt
	22-30	58.9	7.64	-294	21.4	2.5Y. 2.5/1	clay
4	0-9	21.9	7.99	-296	19.3	mix of 2.5Y. 5/4 & 5Y.	clayly silt
	9-16.5	73.1	8.09	-354	19.5	5Y. 2.5/1	clayly silt
	16.5-	31.3	7.84	-301	19.1	mix of 2.5Y. 5/4 & 5Y.	clay
	25.5-36	27.3	7.8	-277	19	2.5Y. 5/4	clay
5	0-3	38.3	7.62	-270	20.1	5Y. 2.5/1	clayly silt
	3-11	4.8	7.82	-287	20.1	Gley4. 5GY 4/1	clay+fine shell
6	0-7.5	107.8	7.84	-384	19.1	Gley2.5 N2.5	clayly silt
	7.5-15	129.5	7.95	-364	19	Gley2.5 N2.5	mainly clay
	15-22.5	57.6	8.01	-300	18.9	5Y. 2.5/1	Clay+little silt
	22.5-30	83.7	8.05	-339	19	5Y. 2.5/1	clay
7	0-8	14.0	7.81	-316	20	5Y. 3/1	clayly silt
	8-11	7.1	7.88	-306	20	Gley4. 5GY 4/1	clay+fine shell
10	0-4	0.7	7.69	-322	19.1	Gley4. 5G 4/1	clayly silt
	4-8	6.2	7.82	-267	19.5	Gley4. 5G 4/1	clay+fine shell
11	0-4	69.3	8.08	-380	19.4	Gley2.5 N2.5	clay+cluster sand
	4-10	46.0	8.02	-390	19.4	2.5Y. 2.5/1	clayly silt +broken shell
	10-19	41.7	7.83	-386	19.5	2.5Y. 2.5/1	mainly clay
12	0-6	4.3	7.47	-348	19.1	5Y. 2.5/1	clayly silt +fine shell
	6-12.5	0.2	7.7	-305	19.3	5Y. 3/1	clayly silt +fine shell

* Sediment Colour:

Gley2.5. N2.5	Black
Gley4. 5GY 4/1	Dark Greenish Gray
Gley4. 5G 4/1	Dark Greenish Gray
2.5Y. 2.5/1	Black
2.5Y. 5/4	Light Oliver Brown
5Y. 2.5/1	Black
5Y. 3/1	Very Dark Gray

Table 5.3 shows the characteristics of the sediment cores collected. The results show that no matter how long the core is, black sediments can always be

found on the top few centimeters and with a dark green or brown-gray layer underneath. Coarse sediments and shell fragments are also commonly found in the cores collected at Inner Tolo Harbour (Locations 9, 10, 11 and 12). The sediment cores were sliced into segments for analysis and the results of pH, Eh, AVS, grain size and sediment colour are shown in Table 5.3.

This vertical pattern of AVS variation has been reported in some previous studies. Peaks were found between 0-15 cm in freshwater sediments (Howard and Evans, 1993, Leonard et al., 1993; Jorgensen, 1977). Beneath the top layer, AVS decreases sharply as a result of pyritization. But at several sampling locations (e.g. locations 1, 2 and 6) of this study, more than one single peak is found. Several layers of sediments with high AVS concentrations were found intercalating with layers with lower AVS concentrations.

To ascertain the controlling factors of such variation pattern, a correlation analysis was undertaken to find out the relationship between AVS and pH, as well as the relationship between AVS and Eh (Table 5.4). Besides, the results of AVS content and characteristics of sediments (colour and grain size) were compared to search of any discernible pattern.

Table 5.4. Correlation of AVS (μmol/g) of pH and Eh of Sediment Cores

Correlation	AVS
pH	-0.40
Eh	0.42

Significance level of the correlation are > 0.05

From Table 5.4, it is clearly seen that the role of pH and Eh in determining AVS concentration is not very important and their correlation are not statistically significant. Therefore, it is nonreliable to depend on these two parameter in explaining the vertical variaiton of AVS.

On the other hand, the present study found that sediment colour and grain size also related to AVS. Firstly, higher AVS concentrations are usually found in black sediment layers (e.g. sediment cores at location 2). Black sediments usually suggest the existence of organic matters (Doyle, 1968; Thode and Jorgensen, 1989) which is one of the primary controlling factor of AVS formation. Furthermore, Doyle (1968) observed that darkening of the sediments is caused by iron sulfide as confirmed by the liberation of H_2S and ferrous iron under treatment of dilute acid.

The effect of grain size on AVS can be reflected in the sediment core collected at location 6. For the sediment layers having the same black colour, it was found that the smaller the grain size, the higher is the AVS content.

5.1.4 Effects of AVS Variation on Metal Bioavailability

As mentioned in Chapter 1, AVS is an important metal binding phase in anoxic sediments such as in the Hong Kong coastal areas. It can scavenge the metals and reduce the amount of metals in the pore water that is available for the

benthic organisms. This section is going to assess the implication of AVS distribution pattern vertically, seasonally and spatially.

As regards the vertical variation of AVS, higher AVS concentrations are usually recorded in the top layers of the sediment cores. Although there is still a considerable amount of AVS in the bottom layer, since metals removed from the water column are deposited on the surface of the sea bottom, toxicity mediation by AVS is most prominent in the top layers.

AVS in the upper layer is not only greatest in amount, it is also most sensitive to seasonal changes. Howard (1992), Leonard and others (1993), pointed out that AVS was lower in cooler months as a result of oxidation. Hong (1992) also postulated that metal bioavailability may increase if the AVS and organic matters are oxidized. However, in the study area, although Eh of the overlying water varies seasonally, the magnitude of change is not large enough to alter the anoxic conditions. Therefore, loss of AVS due to oxidation is unlikely to happen.

Actually, the reduction of AVS concentration is the outcome of the scouring effect of summer and autumn storms. These storms may wash away or cover up the sulfide-rich sediments and reduce the capacity of AVS to react with metals.

Spatially, lower AVS contents are found at sampling locations near the estuary of Shing Mun River, so the capacity of AVS to scavenge metals is relatively smaller at those sampling locations. However, the AVS contents in Shing Mun

River and Inner Tolo Harbour (Table 5.5) is apparently higher (mean = 76.8 μmol/g) than that of other areas. Most importantly, all of the sediment samples (except location 9 in spring) contained AVS concentrations exceed 1μmol/g. Di Toro and others (1990) suggested that the role of AVS is prominent only if the concentration of AVS is greater than 1 μmol/g. Therefore, AVS in the study area is high enough to affect potential metal bioavailability.

Table 5.5. AVS in Sediments of Different Locations in Previous Studies

Description	**Site**	**AVS (μmol/g)**
Marine	♣Black Rock Harbour	175.0
	♣Long Island Sound	15.9
	♣Ninigret (salt water) Pond	2.3
	✷Port Angles Harbour	1.9-50.5
Estuarine	♣Hudson River	12.6
	♥East River	8.8
	※Fox River	13.0-21.6
	✣Limfjorden	20.0 (μmol/ml)
Freshwater	♦Super Fund Site (adjacent to Hudson River)	0.1-75.5
	♥Pequaywan Lake	42.6
	♥West Bearskin Lake	3.6
	♠Caribou Lake	<0.1-9.8
	♠Fish Lake	0.1-6.0
	♠Pike Lake	1.3-36.2
	✣Crosson Lake	0.1-7.7
	✣Gullfeather Lake	0-0.9
	✣Jack Lake	0.2-7.5
	⊗Steilacoom Lake	0.3-4.2
Hong Kong	Shing Mun River and Inner Tolo Harbour	76.8 (7.1 - 164.1)

Sources :

♣ Di Toro et al., 1990
♦ Ankley et al., 1991
♥ Carlson et al., 1991
♠ Leonard et al., 1993
✣ Howard and Evans, 1993
✷ Casas and Crecelius, 1994
⊗ Ankley , 1993
※ Ankley , 1994
✣ Jorgensen, 1977

5.2 ROLE OF AVS IN METAL TOXICITY MEDIATION

The affinity of metals for sulfides has long been recognized (Morel et al., 1973). In reviewing previous studies, Morse and others (1987) stated that "Zn is strongly associated with sulfides in many anoxic waters and sediments.... The importance of Pb interaction with sulfides has been demonstrated in the Cariaco Trench where Pb is scavenged from the water column on iron sulfides. Other heavy metals which have been found to be frequently associated with the sulfide fraction of suspended matter and sediments in anaerobic environment include: Cu, Co, Ni, Cd, As, Sb, Hg and occasionally Mn".

One might wonder whether the sediments contain sufficient AVS to mediate metal activities in the study area. The question can be answered by comparing the metal content to AVS content on a molar basis (i.e. SEM/AVS molar ratio). Furthermore, the effectiveness of AVS in mediating metal toxicity will also be assessed by examining the concentration of labile metals in pore water.

5.2.1 SEM/AVS Molar Ratio

The importance of sulfide as regulator of metal bioavailability and toxicity has been highlighted only in recent years. The pioneers in this field suggested that "no significant mortality occurs if the molar concentration of acid volatile sulfide (AVS) in the sediments is greater than the molar concentration simultaneously extracted metals (SEM)" (Di Toro et al., 1990; Di Toro, et al., 1992; Ankley et al.,

1991; Ankley et al., 1993). The SEM/AVS ratio has been regarded as a valuable indicator of sediment toxicity.

SEM are metals generated during AVS analysis (Di Toro, et al., 1990), and, in this study, Cd, Cu, Pb, Ni, and Zn are taken into consideration. With regard to the results (Table 5.6), the most abundant metal in SEM is Zn which makes up more than 95% of total molar concentration of metals. Pb is the second most abundant metal, followed by Ni and Cu. Cd is the rarest metal, occurring at levels close to the detection limit.

Table 5.6. Variation of SEM (μmol/g) among Sampling Locations

Location	Zn	Cd	Pb	Cu	Ni	SEM sum
1	5.24	0.01	0.57	0.05	0.17	6.03
2	5.28	0.02	0.54	0.14	0.21	6.18
3	6.93	0.02	0.53	0.05	0.49	8.00
4	2.29	0.00	0.18	0.09	0.08	2.65
5	3.53	0.01	0.39	0.08	0.11	4.11
6	2.70	0.01	0.35	0.22	0.13	3.40
7	2.73	0.00	0.33	0.19	0.10	3.35
8	0.65	0.00	0.09	0.07	0.03	0.83
9	0.83	0.00	0.11	0.08	0.03	1.04
10	1.41	0.00	0.19	0.13	0.05	1.79
11	4.19	0.03	0.48	0.80	0.33	5.82
12	1.66	0.00	0.23	0.21	0.07	2.17
mean	3.12	0.01	0.33	0.17	0.15	3.78
*C.V.	0.63	1.01	0.52	1.17	0.92	0.60

* C.V. = Coefficient of Variation

Figure 5.8 shows a pronounced spatial variation of SEM concentrations among sampling locations. Despite the large spatial variability, all sediment

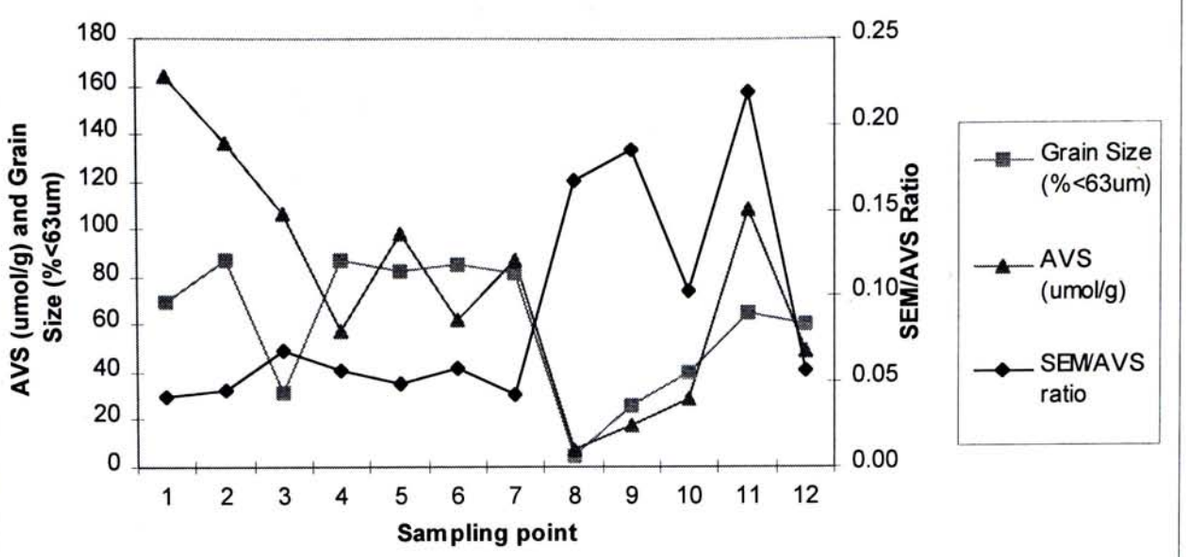
samples have SEM/AVS ratios smaller than 1 for all seasons, and in fact, most of the ratios are below 0.1. In other words, the sediment have adequate AVS to scavenge metals and reduce their bioavailability and hence toxicity to the biota. Indeed, low SEM/AVS ratios of the sediments can be found at most sampling points in the study area, and high SEM/AVS ratios near the estuary, i.e. locations 8,9,10 and 11 (Figure 5.8).

To study the changes of SEM/AVS ratios, the correlation matrix relating SEM/AVS ratio to other sediment properties is presented in Table 5.2. SEM/AVS ratios is strongly correlated to AVS concentration, Eh and grain size of the sediments.

The generally low SEM/AVS ratios in the study area is mainly due to the anoxic environment which provides a favourable environment for AVS formation and at the same time prevents the AVS from oxidation. Since AVS concentration is the denominator in the SEM/AVS ratio, when the concentration of AVS is high, the SEM/AVS ratio will be small.

Grain size is also responsible for the high SEM/AVS ratios that are found near the estuary (locations 8, 9, 10 and 11). At these locations, the sediments are mainly composed of sand and coarse silt, which are usually associated with oxic condition. An oxic environment is unfavourable for the formation of AVS. As a result, AVS concentrations are small, and hence the SEM/AVS ratio is large.

Figure 5.8. Relation between SEM/AVS ratio, AVS and Grain Size



5.2.2 Fraction of SEM in Total Metals of the Sediments

As mentioned in chapter 4, Phase IV (organic matters and sulfides) is the most important metal-binding phase in the sediments. Since AVS is invariably produced in organic-rich reducing environments where organic matters and sulfide are intimately mixed (Warren, 1981), it is difficult to differentiate the amount of heavy metals precipitated with sulfide and organic matters.

To determine the role of AVS in metal mediation, the concentration of SEM is compared with the metal concentration existing in Phase IV (organic matter and sulfide) and the sum of all five phases as extracted by the sequential extraction method. Although it is not appropriate to compare the results obtained by different methods, it can, at least, serve as a reference to show the fraction of total metals associated with AVS.

Table 5.7. Comparison of Concentration of SEM, Fraction IV and Total Metals

	Pb (µg/g)			Cu (µg/g)			Cd (µg/g)			Zn (µg/g)			Ni (µg/g)		
Location	SEM	IV	Total	SEM	IV	Total	SEM	IV	Total	SEM	IV	Total	SEM	IV	Total
1	116.74	5.94	107.48	2.77	43.10	58.17	1.24	0.71	2.25	342.66	78.24	357.82	9.96	5.25	16.03
2	111.14	4.08	105.64	9.02	77.66	106.03	1.67	0.71	2.63	345.13	79.28	362.25	12.23	6.08	19.83
3	109.84	7.44	114.41	2.96	198.64	231.40	1.89	0.63	1.58	452.81	132.96	487.67	28.56	11.19	27.26
4	37.25	1.27	42.56	6.01	19.51	34.84	0.37	0.23	1.00	150.11	24.26	157.36	5.01	1.44	6.23
5	80.79	6.69	88.25	5.16	59.30	80.48	0.84	0.49	1.74	230.99	54.57	273.84	6.21	5.13	13.90
6	72.94	1.19	84.14	13.97	64.85	91.06	0.88	0.48	1.64	176.54	40.97	219.19	7.37	6.12	16.36
7	67.76	4.61	77.11	12.27	44.23	63.69	0.76	0.40	1.48	178.11	38.11	217.47	5.99	4.68	13.92
8	17.61	0.38	22.81	4.37	5.58	11.03	0.28	0.07	0.20	42.57	4.82	51.49	1.84	0.30	2.52
9	21.94	1.76	32.82	4.87	9.50	16.08	0.15	0.09	0.16	54.11	12.85	80.49	1.45	1.19	4.46
10	30.11	1.95	49.96	6.36	24.12	37.20	048	0.20	0.58	69.01	17.61	103.54	2.07	2.50	7.52
11	98.74	2.51	62.88	50.52	75.90	105.93	2.84	0.40	1.37	273.97	38.32	170.23	19.30	7.64	18.68
12	46.74	3.03	59.25	13.31	37.78	54.95	0.57	0.25	1.01	108.58	25.98	138.80	4.05	4.45	11.67

From the comparison in Table 5.7, it can be observed that the concentrations of Zn, Pb, Cd and Ni in SEM exceed the concentrations extracted from Phase IV of the sequential extraction method and in some cases, SEM concentration even approaches the total metal concentrations. These results suggest that metals from other binding phases, such as carbonate and Fe-Mn oxides, are also included in SEM.

Even the metals from other binding phases are included in SEM, SEM contents are still less than the AVS equivalence. Therefore, the SEM/AVS ratio at all the sampling locations is smaller than 1 throughout the study period. As reported in previous studies, no significant mortality of marine organisms is expected if the SEM/AVS ratio is less than 1. The findings strongly indicate that the study area is free from acute metal toxicity.

5.2.3 Labile Metals in Pore Water

Measurement of the labile metals in the pore water can be an indicator of the effectiveness of AVS in controlling metal bioavailability. If SEM exceeds AVS content, the binding ability of AVS will be used up and the excess metals will be present in the pore water. The metal concentrations in pore water can thus reflect the amount of surplus metals (Ankley et al., 1994; Casas and Crecelius, 1994). Analysis of metals in pore water is a complementary approach to assess not only the presence, but also the extent of metal toxicity, in sediments.

Table 5.8. Mean, Range and Coefficient-of-Variation of Labile Metals (μg/l) in Pore Water

Labile Metals	Mean	Range	Coefficient of Variation
Zn	309.0	0.0 - 1347.3	0.84
Cd	1.5	0.0 - 42.3	4.33
Pb	103.6	0.0 - 2754.9	4.34
Cu	6.3	0.0 49.1	1.91

From the result (Table 5.8), it can be seen that labile metals are present in the pore water, even when SEM/AVS ratio is smaller than 1. Zn is the most abundant labile metal in the pore water, followed by Pb, Cu and Cd.

The high Zn concentration in the pore water can perhaps be explained by extraction method and the solubility of ZnS. Bufflap and Allen (1995) showed that centrifugation produced a higher and more variable amount of Zn. This is because Zn has a relatively lower affinity for clay and organic matters, as a result of which Zn is dissociated during centrifugation from the binding phases.

High solubility of ZnS may also account for the high labile Zn in pore water. The occurrence of metals in the sediments is controlled by the solubility product (Ksp) of metals. The solubilities of various metal sulfides are not the same and among them ZnS has a higher solubility. As ZnS is more soluble than CdS, PbS and CuS, Zn can easily exchange with other metals and be released to the pore water.

Based on the existence of labile metals in the pore water alone, one may jump to the conclusion that AVS is not effective to mediate metals toxicity in the study area. However, one should approach the problem by evaluating the fraction of labile metals as a fraction of the total metals present in the sediment and pore water. This fraction reveals the amount of metals in the sediments that is not bound.

Table 5.9. Average Percentage of Labile Metals in Total Metals of in the Water-Sediment Matrix

Location	Zn	Cd	Pb	Cu
1	0.10	0.02	0.01	0.00
2	0.09	0.01	0.09	0.00
3	0.01	0.16	0.19	0.00
4	0.33	0.02	0.03	0.02
5	0.22	0.02	0.02	0.02
6	0.27	0.00	0.02	0.00
7	0.21	0.01	0.03	0.00
8	0.00	0.00	0.00	0.00
9	1.10	4.45	0.02	0.04
10	0.36	0.00	0.04	0.03
11	0.34	0.30	2.09	0.00
12	0.48	0.11	0.21	0.04

From Table 5.9, it can be seen that with very few exceptions, the amount of various labile metals in pore water is generally below 0.4 % of the total metal in water-sediment matrix. From this perspective, one may conclude that AVS does play an effective role in mediating metal.

5.2.4 Dissolved Sulfide in the Pore Water and the Overlying Water

Dissolved sulfide in pore water also plays a role in metal toxicity mediation. Dissolved sulfide in sediments is of course important, however, it is not measured directly with an electrode, as suggested by Howard (1992), because of scratching the electrode membrane. Instead, dissolved sulfide in pore water is measured. The concentrations of dissolved sulfide in the pore water vary greatly among locations (Appendix G) with a mean of 16.3 mg/l and range between nondetectable to 180.3 mg/l. However, the concentrations of dissolved sulfide in the overlying water are much smaller than that in the pore water. Dissolved sulfide, especially in the surface water, is in an unstable condition and is easily lost from the water through volatilization. Therefore, dissolved sulfide in pore water is believed to play a much more active role in binding metals than that in the overlying water.

Howard (1992) stated that most of the previous AVS studies eliminated the dissolved sulfides by subtracting them from the total AVS value (For examples, Ankley et al., 1991a; Di Toro et al., 1990; Carlson et al., 1991, etc.). However, dissolved sulfides are more available for metal interaction than those in solid phase. Therefore, if only solid phase AVS measurement is taken into consideration, reactivity of the sulfide pool may be underestimated. Therefore, a total AVS measurement, rather than just the solid phase AVS, would give a more realistic measurement of the sulfides available for reaction with metals (Howard, 1992).

5.3 Conclusion

There is a clearly discernible spatial variation of AVS concentration at different sampling locations. Higher AVS contents are recorded in upstream area, and lower AVS concentrations near the estuary. This distribution pattern suggests that sulfate is not the limiting factor of AVS formation. Other sediment properties, namely organic carbon, grain size, and Eh are the more important determinants of AVS concentrations. Therefore, lower AVS concentrations are recorded at the estuary where the sediments are coarser, lower in organic content and higher in Eh.

AVS concentration also varies among seasons. The amount of AVS in the sediments is in the sequence of summer > spring > winter > autumn. As already explained, the increase of water temperature from spring to summer is responsible for the increase in AVS in summer, whilst the loss of organic matters after storm flushing is the main reason for the decrease of AVS content in autumn.

Furthermore, AVS exhibits vertical variation down the sediment cores. AVS concentrations are generally higher in upper layers. Grain size and colour are good indicators of the AVS content.

Notwithstanding the variability of AVS concentration, none of the sampling locations has SEM/AVS ratio greater than 1. Even when the metals from other metal binding phases are extracted and included in SEM, SEM is still smaller than the content of AVS. In other words, there is adequate capacity of AVS to scavenge

metals in the sediments. Therefore, one can conclude that the study area is not suffering from acute metal toxicity. On the other hand, although labile metals can be detected in pore water, the fractions of labile metals in pore water is only a very small fraction of the total amount present. Furthermore, it is also worthwhile to note that the dissolved sulfide in pore water can take part in metal mediation and regulate the amount of metals in the pore water that will ultimately be bioavailable to the biota.

CHAPTER 6

CONCLUSION

6.1 INTRODUCTION

This research investigates the movement, fate and potential risks, of heavy metals in a tidal channel and its adjoining sea inlet in Hong Kong. The situation in the Shing Mun River and the Inner Tolo Harbour is not unique. In many coastal cities of the world, one can find many similar cases in which industrial effluents bearing substantial amount of heavy metals are poured into the sea through natural and artificial channels. There are many questions which environmental managers may ask. The first is to what extent these metals exist in the free ionic "labile" form which is known to be more toxic than the non-labile fractions. Then, one would ask whether the channel is a "drain" or a "sink" or if it is both. If it is both, when would it become a drain or a sink and change from one to the other? In the sink, what binds the heavy metals and how strong is the binding? Can this binding be so perturbed by the natural climatic and hydrologic variations throughout the year that the heavy metals held in the sediments be remobilized again? If the metals are indeed remobilized, will they re-enter the overlying water column and will they pose any significant risk to the biota and mankind?

These are those questions this thesis set out to explore and answer. As in many other studies, the research has raised more questions than it has answered. This chapter will summarize the major findings of the study and highlight unresolved issues that merit further investigation. It is hoped that based on these findings one could build a more comprehensive picture of the dynamics and fate of heavy metals in a near-shore environment that could help formulate better environmental strategies.

With the above questions in mind, this study has embarked on a one-year sampling program that measures the concentration and speciation of heavy metals in the channel bottom sediments as well as in the overlying water. A number of other physico-chemical parameters which are known to affect metal concentration are also measured and, so is the acid-volatile sulfide in the sediments.

6.2 MAJOR FINDINGS

Located in an area with a number of electronic and electroplating industries, the Shing Mun Channel receives significant quantities of industrial effluents containing heavy metals for over a decade. Although the discharge of heavy metals has been decreasing in recent years as a result of tightening pollution control, the water in the channel and inner harbour still contains a significant quantities of Cu and Zn, at levels comparable to those found in the most polluted areas of Hong Kong. However, not all of these metals occur in the free ionic "labile" form. With the exception of Zn, labile metals account for only 10 to 30% of the total metals

present. The remaining presumably have been complexed by inorganic and organic ligands in the sea water. As metals occurring in the labile form are in the ppb range, the risks posed to the aquatic organisms are presumably small.

As compared to the water column, the bottom sediments are invariably enriched with various heavy metals. They have been removed from the water column by adsorption, precipitation and settlement of biogenic materials. In this sense, the channel bottom is a sink of metals. As in the overlying water, the abundance of metals in the sediments are in the sequence of Zn (average=218.3 μg/g), Cu (average=74.2 μg/g), Pb (average=70.6 μg/g), Ni (average=13.2 μg/g) and Cd (average=1.3 μg/g). In comparison with previous studies on contaminated sediments, metals in these concentration ranges are considerably high. As the bottom sediments in Hong Kong are frequently disturbed or dredged, the fate of the metals in sediments merits close attention.

Given the potential risk posed by the metals in the sediments to the biota, an in-depth investigation has been undertaken to ascertain the chemical speciation of the metals using the sequential extraction method and to determine the properties of the sediments. It was found that only about one-third of the metals exist in the stable residual crystalline forms. Of the remaining, only a very small proportion is associated with the exchangeable and carbonate fractions and the majority are either associated with organic matters, sulfides or Fe-Mn oxides.

The water and sediments in the channel and inner harbour can be envisaged as an integrated system in which the sediment pool is both a sink for the metals as well as a source of pollution at certain times of the year. An examination of the physico-chemical properties of the overlying water indicates that whilst the properties of the surface water vary from season to season, that of the bottom layer change much less. At certain times of the year, particularly in autumn, the differences between the surface and bottom are so great and the change is so abrupt that water stratification is evident. When this occurs, replenishment of oxygen to the bottom layer is significantly impeded and the water close to the sediment interface is so deprived with oxygen that almost an anoxic state is reached. This favours the reduction of sulfate, the formation of sulfide substances, and the binding of metals to the sulfides in the sediments.

Substantial amounts of acid volatile sulfide substances are thus found in the bottom sediments of the study area. The concentrations of AVS found in the study area are higher than those found in the many other areas reported in the literature. It has been found that in the Shing Mun Channel, because it is a tidal river, the supply of sulfate is not a limiting factor for AVS formation. The upstream stretch of the channel is particularly high in AVS. These are locations where the sediments are fine and the organic matters rich. Both conditions provide a favourable environment for the formation of AVS. On a molar basis, it has been found that there is more AVS in the sediments than is needed to interact with, and to moderate the toxicity of, the sediment associated heavy metals. This applies to all sampling locations,

although the ratio approaches 1 towards at the estuary of the river channel where the sediments are relatively coarse.

The Shing Mun River is a tidal channel where the stream and sea water meet and the relative importance of the two depends on the season and the location. In summer and at upstream locations, fresh water dominates. However, fresh water gives way to sea water in the downstream direction in the dry season. During the summer rainy season, it was observed that the influx of stream could bring about significant changes to the pH and salinity of the surface water, and at the same time enhance the formation of stratification in the water body.

Of the various changes caused by rainstorms, the decrease in salinity is not likely to bring about metal remobilization. Theoretically, a drop in the pH may enhance metal release. However, the magnitude of pH change that takes place in the bottom layer is probably not sufficient to bring about any significant metal remobilization. In any case, only a small amount of metals in the sediments exist in the exchangeable or carbonate forms that are readily remobilized through pH changes. The Eh of the bottom water, on the other hand, may enhance the dissolution of metals associated with Fe-Mn oxides. At the same Eh value, Zn, Cu, Pb, Ni and Cd can also be partitioned with organic matters and sulfides.

During the rainy season, the influx of fresh water in the study area does not appear to significantly affect the concentration of AVS. Hence, it does not affect the role of AVS in mediating metal toxicity. As previously said, the Eh of the bottom

water is always kept in a state approaching anoxic conditions, and this prevents the loss of AVS due to oxidation. The drop of AVS in autumn was probably caused by the deposition of fresh sediments brought down by the floods than by the oxidation process.

The AVS in the study area plays a very significant role in mediating the metal toxicity. As mentioned, the bottom sediments in the study area are enriched with heavy metals, but they are also high in AVS. Heavy metals are known to have a positive relationship with fine sediments and organic matters, both of which may enhance AVS formation. Therefore, where the concentration of metals are high, the AVS is high too. The issue that remains is whether there is sufficient AVS to counteract with the metals.

A multi-thronged approach has been adopted to tackle the above issue. The first approach looks at the SEM/AVS ratio. It is generally held that the molar ratio between the SEM and AVS is an indication of sediment toxicity. In the study area, the ratio at all sampling locations is smaller than one throughout the study period, suggesting that there is no acute metal toxicity problem. In other words, most of the metals present in the sediments can be moderated by sulfides and so very little metals are readily available to the aquatic life. The role of AVS in partitioning metals is also indirectly substantiated by the analytical results of the pore water extracted from the sediments. It has been found that whilst some labile metals, particularly Zn, still exist in the pore water, their occurrence only accounts for a very small proportion (0.1 - 0.4 %) of the total metal present in the water-sediment pool

matrix in the channel bottom. Furthermore, the pore water metal content is much less than the concentration of metals in the overlying water. The presence of dissolved sulfide, sometimes at concentrations in excess of 10 mg/l, also indicates the existence of sulfides that can readily react with metals to reduce the toxicity.

In summary, the results of this study suggest that both the water and the sediments in the study area contain elevated levels of heavy metals. However, only a small proportion of the metals in the water column exist in the labile form. Whilst the sediment metal contents are high, the metals are largely associated with organic matters, sulfides and Fe-Mn oxides. The AVS pool is so large that there is more than adequate capacity to react with the metals to mediate the toxicity. In spite of the dynamic nature of the hydrological conditions in the tidal channel and the inner harbour, the season to season variations in the water physico-chemical properties do not bring about sufficient changes to effect any significant remobilization of metals. Hence, most of the metals are not readily available to the biota and the risks posed to the marine organisms are not great as the total metal concentration may suggest.

6.3 PRACTICAL IMPLICATIONS OF THE FINDINGS

What are the implications of the findings in environmental management? As afore-mentioned, estuaries have attracted a great deal of attention as they are places rich in marine life and where the environment is dynamic and constantly-changing.

The findings of this study do suggest that whilst the pollution levels are high, the channel and sea bottom is a sink for the metal pollutants. The sink also provides a large pool of AVS which can react with the metals, thereby mediating metal toxicity. This reinforces the notion, advocated by many researchers in the early 1980s, that a single measure of the total metal concentration is not a reliable indication of the potential metal toxicity. There is a need to look, not only at the chemical speciation, but also at other co-existing substances, such as AVS, that may mediate the metal toxicity.

It follows that there is a need to re-examine the sediment quality criteria which are largely based on the total metal content and/or the amount of metals found in the sediment elutriate. For reasons given above, the total concentration is not a reliable measure of toxicity. Furthermore, because the conditions of the elutriate test is not the same as those at the water-sediment interface, the results of the elutriate test may not reflect the actual amount of metals that could be remobilized from the sediments. In light of these findings, there appears a need to re-define the method for assessing sediment toxicity.

This is not to imply that bottom sediments would never pose any problem to the environment. In fact, bottom sediments have to be periodically dredged and disposed of elsewhere for navigation and engineering reasons. The disturbances to these bottom sediments and the subsequent disposal of the dredged materials at locations where the physico-chemical conditions are different from that of the source area may introduce factors that may enhance remobilization of metals. This is an

issue outside the scope of this study but is one too important in the practical world to ignore.

The current approach adopted in Hong Kong to assess potential metal toxicity in marine sediments in Hong Kong is overly simplistic. The criteria for classifying marine sediment for disposal are based merely on the total concentration of metals (Lau and Bradley, 1991). Neither the chemical speciation nor the AVS has been considered. Given the large quantities of contaminated sediments which require disposal because of the many large infrastructure projects, it is high time for the government to rethink the contaminated sediments disposal strategy in the light of recent scientific findings.

6.4 SUGGESTIONS FOR FURTHER STUDIES

Given the time and resource constraints, this study can only focus on a few issues which are key to the understanding of the metal pollution problem. As earlier said, this study has raised more problems than provided answers. The most notable unresolved issues are the high levels of labile zinc in the water column and the occurrence of labile metals in the presence of dissolved sulfide in the sediment pore water. Another one is whether there are other major metal binding phases, other hand AVS, in the sediments.

Of course, if one were to start the research from afresh, a different approach could be followed. The limitation of sampling the water and sediment only quarterly is acknowledged. To fully capture the dynamic changes in the near-shore environment, one may like to undertake additional sampling tasks immediately after heavy rainstorms when changes in the water phyisco-chemical properties are expected to be the greatest.

One could also go a step further to validate the results of this study by looking actually at the toxicity effects on the biota, either through bioassay, or through toxicity tests with algae, bacteria and other target organisms. This is badly needed to substantiate the findings of this study, but would be a study of its own.

In undertaking the above toxicity tests, one should not lose sight of the fact that heavy metals are not the only substances in the sediments that may cause toxicity. In a polluted sea inlet such as the study area, there are bound to be other co-existing substances which are toxic. The micro-organic pollutants, such as PAH and TBT, are known to be present in marine sediments in Hong Kong. Furthermore, the dissolved sulfide and ammonia may also contribute to the toxicity. What complicates the picture is the observation that wherever the metals and toxicants are high, the AVS is high too. Isolation of these various toxicants is a challenging task for the ecological toxicologist.

The last, but not the least, topic that merits close investigation is the ultimate fate of heavy metals and AVS in the bottom sediments following the improvement

in the quality of the overlying water. In the past, much attention has been given to the fate of heavy metals in disturbed contaminated sediments. In the future, one may ask what could happen to these metals if the overall environmental quality improves but the contaminated sediments are allowed to remain undisturbed. The Shing Mun Channel is a case in point, where the overall water quality has been improving since the introduction of stringent pollution control measures a few years ago. There are signs that the heavy metal load has dropped, the organic load has dwindled and the dissolved oxygen has bounced back. This trend will continue in Hong Kong as well as in many other places and one may wonders what will be the fate of the metals in the bottom sediments. It is an important issue that demands in-depth investigation.

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Appendix A. AVS Extraction and Detection Method

AVS Extraction

Sulfide extraction is mainly conducted by a combination of the purge and trap (Di Toro, 1990) and the diffusion method (Brouwer and Murphy, 1994).

Diffusion method for the determination of reduced inorganic sulfur species in sediments has been described by Brouwer and Murphy (1994). This method employed two flasks one inside the other. The outer flask was a 500ml vial closed with a cap into which a polyethylene turbing was inserted. About 4g wet sediment and 25ml deaerated distilled water were placed in the 500ml vial. A smaller vial with 12.5ml SAOB was placed inside the vial. The cap was then sealed. 5ml 6M HCl from a bottle top dispenser was added to the sediment. The assembled vials were shaken by a wrist action shaker at a slow speed for 1 hour. The H_2S evolved then diffused into and was absorbed by the SAOB solution. The sulfide ion concentration in the trap solution was measured with a sulfide ion selective electrode (Orion 90-02) and a digital ion-analyzer.

The optimum time for diffusion and absorption was evaluated by Brouwer and Murphy (1994). Their data indicated that diffusion and absorption processes are very rapid and 1hour is adequate for the diffusion step. On the other hand, in order to avoid release of sulfides from less reactive species such as greifite, final concentration of our samples is 1M HCl which is closed to 0.8M recommended by Brouwer and Murphy(1994) and 0.5M recommended by Cutter and Oats (1987).

This passive diffusion technique is less time-consuming than the purge and trap method. It requires less equipment and yields at least 10% more AVS than the common purge and trap method. (Brouwer and Murphy, 1994).

In this study, the diffusion method was used and followed by the purg and trap method. This step was taken in order to collect any residual sulfide in the slurry. The purge and trap process involved the purging of the slurry by nitrogen gas for 15 minutes. The H_2S evolved was diffused into and aborbed by the SAOB solution.

AVS Detection

The sulfides released and absorbed were determined mainly by selective sulfide specific electrode method in conjunction with a double junction reference (Orion 90-02). The detection limit of the method is 0.5 μmol/g (Di Toro, et al., 1990) to 0.01 μmol/g of sediment with a high degree of precision and accuracy. Moreover, the SAOB can also be used to stabilize free sulfide ions in sediment subsamples so that solid phase and dissolved AVS concentrations can be separated. (Criag and Moreton, 1982)

All reagents were of analytical reagent grade: Deaerated distilled water was used throughout the experiment. 1 liter sulfide antioxidant buffer solution (SAOB) contained 100ml 10M NaOH, 35g ascorbic acid and 67g EDTA. EDTA was used to adjust the ionic strength, ascorbic acid serves as an anti-oxidant, and the high alkalinity converts hydrogen sulfide and hydrosulfide ions into divalent sulfide ions which were detectable by the electrode.

The sulfide stock solution, was prepared using freshly washed sodium sulfide crystals. Its concentration was determined weekly by an iodometric titration with 0.025M sodium thiosulfate. Dilution were prepared daily in SAOB solution over the range of 10^{-1} to 10^{-6} M for calibration of the ISE. Cariag and Moreton (1982) recognized that the use of SAOB to trap sulfide ions is a more precise, and less time consuming than iodometric methods.

Calibration of the sulfide electrode and meter followed the manufacturer's recommendations using sulfide standards prepared in SAOB reagent diluted 1:1 with distilled water. The contents of each sulfide transferred into a 50ml polyethylene beaker and stirred under minimum agitation to avoid diffusion of air into the solution and to minimize oxidation of the sample during the measurement (Allen and others, 1991; Allen and others, 1993)

Appendix B. Sequential Extraction Method for Metals Speciation Analysis

In sequential extraction, the sample is treated with a succession of reagents intended to specifically dissolve different sediment phases. Partitioning of particulate trace metals was classified into five fractions: exchangeable, bound to carbonates, bound to Fe-Mn oxides, bound to organic matter, and residual. The first four stages of sequential extraction are introduced by Tessier and others (1979), while the digestion method in the final stage had been modified.

The selective extraction was conducted in 50ml polypropylene centrifuge tubes to minimize the loss of solid material. 3-4g wet sediment were put into the centrifuge tube and under the following steps:

(1) Exchangeable
The sediment was extracted at room temperature with 10ml of wither magnesium chloride solution (1M $MgCl_2$, pH 7.0) with 1 hour continuous agitation.

(2) Bound to Carbonates
The residue from (1) was leached at room temperature with 10ml of 1M NaOAc adjusted to pH 5.0 with acetic acid (HOAc). Continuous agitation was maintained.

(3) Bound to Fe-Mn Oxides
The residue from (2) was extracted with 10ml 0.04M $NH_2OH \cdot HCl$ in 25% (v/v) HOAc. The latter experiment were performed at 90±3°C with occasional agitation for 6 hours.

(4) Bound to organic matter and sulfide
To the residue form (3) were added 3ml of 0.02 M HNO_3 and 5ml of 30% H_2O_2 adjusted to pH 2 with HNO_3. the mixture was heated to 85±2°C for 2 hours with occasional agitation. A second 5ml aliquot of 30% H_2O_2 was then added and the sample would be heated again to 85±2°C for 3 hours with intermittent agitation. After cooling, 5ml of 3.2M HN_4OAc in 20% (v/v) HNO_3 was added and the sample would be agitated continuously for 30min. The addition of NH_4OAc was designed to prevent adsorption of extracted metals onto the oxidized sediment.

Between each successive extraction, separation was effected by centrifuging at 7000rpm for 15min, whereas the residue was washed with several milli liter of deionized water. Then it would be centrifuged for 10 more minutes. This second supernatant was discarded. The supernatant from the two centrifugations were put into a 25 ml volumetric flask and diluted to mark. All glassware used for the experiments was previously soaked in 14% HNO_3 (v/v) and rinsed with deionized water. All reagents used in this study were of analytical grade.

(5) Residual

The residue after 4-phase extraction will be washed into the Teflon vessel of the microwave digestor. 6ml HNO_3, 2ml $HClO_4$, and 6ml HF were added into each vessel and digested for 60min in a microwave digestor. After digestion, the solid will be washed into a Teflon beaker. Then, it was evaporated to near dryness. The beakers were then cooled down and 5ml HCl and 5ml deionized water were added into the beaker and boiled until bubbles appeared. The samples were filtered through no.44 ashless filter paper and diluted to 25ml.

The resulting solution from the above five stages was then analyzed by flame and furnace atomic absorption spectrophotometry for trace metals using the standard addition technique.

Appendix C. Instrument List for the Experiments

Determinants	Equipment
pH	Field: Digi-Sense Digital pH (ATC)/mv/ORP meter (C-P model 5985-80) Corning M90 pH sensor and meter Lab.: Orion Ross pH Electrode Orion model 720A benchtop pH/ISE meter
Eh	Field: Digi-Sense Digital pH (ATC)/mv/ORP meter (C-P model 5985-80) Lab.: C-P ORE Redox Combination Electrode Orion model 720A benchtop pH/ISE meter
DO	Oxygen probe YSI model 57 Oxygen Meter
Suspended Solid	Field: Partech 7000-3RP Portable Suspended Solids Analyser Partech Type 7000/PS/Series Sensors
Salinity	Field: Orion model 140 Conductivity / Salinity Meter Lab.: YSI model34 Conductance-Resistance Meter
Dissolved S^{2-}	Shimadzu Recording Spectrophotometer UV-160A Orion model 90-02 Double Junction Reference Electrode Orion model 94-06 Sulfide Ion Electrode
TOC	Shimadzu 5000A Total Organic Carbon Analyser Astro model 2001 Computer Control TOC Analyser
AVS	Orion model 90-02 Double Junction Reference Electrode Orion model 94-06 Sulfide Ion Electrode Orion EA940 Expandable Ion Analyser Burrell Wrist Action Laboratory Shaker
SEM	Varian (spectrAA-300) Atomic Absorption Spectrometer
Labile Metals	Metrohm Voltam(pero)metric analyser (ASV) Metrohm UV-Digester
Total Metals	Varian (spectrAA-300) Atomic Absorption Spectrometer

Appendix 3. Instrument List for the Experiments (Cont.)

Determinants	Equipment
Speciation of Metals	Varian (spectrAA-300) Atomic Absorption Spectrometer Julabo Shaking Water Baths Naglene Centrifuge Ware CEM model MDS-2000 Microwave Digester MSE Super Minor Centrifuge Burrell Wrist Action Laboratory Shaker
Grain Size	Hamilton Beach Stirrer US Standard Testing Sieve No.230 (63μm) Fritsch Wet Sieving Shaker
Pore Water Samples	Naglene Centrifuge Ware Centrifugation Machine
Sediment Samples	Wildco-Ekman Bottom Dredge
Overlying Water Samples	Wildco-Alpha Bottles Horizontal Water Sampler
Field Data Convection and Storage	Campbell 21X Micrologger

Appendix D. Monthly Total Rainfall and Mean Temperature of 1995

Month	Total Rainfall (mm)	Mean Temperature (°C)
January	21.1	16.1
February	33.1	15.1
March	32.4	17.9
April	76.3	22.5
May	20.8	26.0
June	243.9	28.7
July	668.7	28.0
August	1090.1	27.4
September	81.4	27.6
October	476.9	25.3
November	1.8	21.2
December	7.9	17.4

Source : Hong Kong Monthly Weather Summary, Royal Observatory

Appendix E. Analytical Results of the Overlying Water

Table E-1. Analtyical Results of the Water in Spring

Location	B/S	pH	Eh (mv)	Temp (°C)	DO (mg/l)	DO (%)	Sal. (ppt)	S. Solid * (mg/l)	S * (mg/l)	TOC (mg/l)	labile Metals (μg/l)				Total Metals (μg/l)				
											Zn	Cd	Pb	Cu	Zn	Cd	Pb	Cu	Ni
1	S	8.04	304	16.0	7.10	71.7	18.4	496	0.98	9.32	721.34	0.06	2.98	27.06	750.00	5.26	23.00	47.18	7.31
	B	7.84	73	17.0	5.95	61.3	27.6	340	1.98	4.01	271.21	0.86	2.35	2.19	294.00	5.13	33.00	39.40	11.52
2	S	8.33	-35	16.0	8.89	89.8	22.5	406	1.08	6.65	287.49	0.51	1.69	ND	355.00	5.35	12.00	27.22	2.24
	B	8.13	-29	17.0	7.30	75.5	30.7	232	1.18	1.95	829.76	0.24	2.40	3.22	851.00	3.03	25.00	36.30	0.14
3	S	8.14	-98	17.0	5.98	61.6	25.0	320	0.19	5.49	282.63	0.14	2.01	2.30	361.00	3.28	20.00	29.36	2.13
	B	7.96	-54	17.5	5.80	60.4	29.1	370	1.98	2.34	490.94	0.22	2.30	4.25	568.00	2.96	11.00	39.18	5.22
4	S	8.30	-27	16.0	7.78	78.6	26.9	304	0.58	4.51	403.62	0.20	1.52	26.67	367.00	2.69	11.00	34.78	1.64
	B	8.13	-32	18.0	7.17	75.5	30.3	250	1.38	1.70	221.32	0.09	1.88	1.91	319.00	2.71	20.00	29.52	2.33
5	S	8.26	11	17.0	9.36	96.5	28.3	390	0.58	3.48	332.71	0.30	2.22	1.90	428.00	3.28	13.00	33.52	0.35
	B	8.12	1	18.0	5.82	61.3	26.9	241	1.18	1.40	296.86	0.10	1.81	2.43	413.00	3.28	6.00	32.14	1.00
6	S	8.47	-30	18.0	9.40	98.9	28.8	248	0.88	3.09	471.66	0.33	2.06	2.48	642.00	2.33	51.00	39.54	0.76
	B	8.11	-33	18.0	6.20	65.3	30.9	217	2.67	1.62	362.42	0.36	2.25	2.76	529.00	2.43	16.00	44.06	0.29
7	S	8.30	-49	17.5	7.85	81.8	28.5	183	1.48	1.59	810.28	1.46	2.30	3.94	801.00	2.05	26.00	30.44	0.85
	B	8.17	-50	19.0	6.25	67.2	31.8	216	0.98	0.69	266.43	0.56	2.45	2.16	407.00	3.57	32.00	36.84	0.46
8	S	8.01	-42	18.0	5.10	53.7	30.8	210	1.38	1.15	412.62	0.84	2.03	2.45	531.00	3.25	28.00	37.78	2.95
	B	8.11	-36	18.0	5.93	62.4	31.3	229	0.98	0.85	576.86	0.10	2.20	2.51	722.00	2.36	2.00	34.86	3.83
9	S	8.27	-6	19.0	8.04	86.5	30.5	219	1.38	2.00	272.61	0.08	2.16	3.10	403.00	5.73	30.00	36.32	1.11
	B	8.22	6	18.0	7.13	75.1	31.9	244	0.38	0.86	267.04	0.22	2.24	3.87	407.00	6.10	21.00	43.66	0.85
10	S	8.37	26	18.0	8.88	93.5	31.3	214	1.18	1.07	424.28	0.05	2.18	2.31	611.00	7.63	25.00	56.22	2.27
	B	8.16	25	18.5	6.11	65.0	32.7	238	0.98	1.12	548.87	0.19	2.48	3.30	581.00	5.21	26.00	31.50	0.82
11	S	8.27	7	19.0	8.15	87.6	31.1	240	0.78	1.45	544.28	0.05	2.27	2.39	669.00	4.28	19.00	35.20	5.19
	B	8.05	-45	18.0	6.73	70.8	32.8	248	0.58	1.02	334.81	0.18	2.34	2.74	461.00	2.67	23.00	30.60	4.92
12	S	8.23	-51	19.0	8.63	92.8	30.4	220	1.78	2.35	579.32	0.27	2.88	2.72	809.00	2.61	25.00	38.78	5.44
	B	8.17	-30	19.0	5.17	55.6	31.4	250	1.98	1.18	611.87	0.56	2.42	5.02	854.00	4.13	27.00	37.88	5.34

* S = Dissolved Sulfide / S. Solid = Suspended Solids
ND = Non Detectable

Table E-2. Analtyical Results of the Water in Summer

Location	B/S	pH	Eh (mv)	Temp (°C)	DO (mg/l)	DO (%)	Sal. (ppt)	S. Solid * (mg/l)	S * (mg/l)	TOC (mg/l)	labile Metals (μg/l)				Total Metals (μg/l)				
											Zn	Cd	Pb	Cu	Zn	Cd	Pb	Cu	Ni
1	S	7.23	171	30.7	5.07	66.7	28.9	379	0.01	ND	282.93	0.30	4.82	7.24	205.00	1.50	43.00	39.20	1.46
	B	7.64	-282	30.3	0.07	9.1	30.6	411	0.93	ND	214.56	0.08	3.57	16.77	170.00	1.02	8.80	33.30	5.61
2	S	7.60	106	30.3	7.79	101.2	28.2	282	0.01	1.78	244.37	ND	2.29	2.24	204.00	1.31	6.60	37.50	15.72
	B	7.71	-234	30.4	0.20	2.6	27.1	337	0.02	ND	357.26	ND	3.34	6.14	254.00	0.66	0.00	25.04	5.76
3	S	7.38	136	30.2	6.82	88.6	24.3	297	0.00	ND	343.03	0.30	3.86	9.92	252.00	1.01	1.80	31.22	7.41
	B	7.83	-128	30.6	4.81	63.3	31.5	267	0.01	ND	170.58	ND	2.34	4.53	158.00	1.30	21.30	34.66	3.70
4	S	7.50	232	30.1	6.44	83.6	28.5	259	0.00	ND	246.31	ND	3.59	7.76	178.00	0.98	21.10	20.68	0.65
	B	7.75	-106	30.7	4.23	55.7	31.8	342	0.00	ND	283.58	ND	3.67	6.80	176.00	0.81	7.10	47.56	6.70
5	S	7.75	171	30.2	7.53	97.8	29.2	259	0.00	1.57	207.76	0.39	2.68	7.23	179.00	0.58	6.60	25.52	1.11
	B	7.90	-81	29.7	7.33	95.2	31.9	281	ND	ND	253.28	0.18	3.08	6.89	175.00	0.62	21.10	37.30	2.59
6	S	7.71	166	29.7	6.61	85.8	28.1	210	ND	1.58	206.28	0.12	2.70	6.20	174.00	0.54	6.60	27.80	3.78
	B	7.92	-79	29.8	6.73	87.4	31.8	221	ND	ND	233.10	0.45	3.27	6.66	172.00	0.44	0.00	37.22	4.24
7	S	7.80	198	29.7	7.58	98.4	28.5	215	0.00	1.66	234.49	0.02	3.19	6.99	158.00	0.50	0.00	35.32	4.35
	B	7.99	-63	29.6	6.77	87.4	32.0	265	0.02	ND	266.94	0.11	2.61	5.30	184.00	0.54	59.40	38.88	3.66
8	S	7.64	154	29.5	6.75	87.1	25.5	212	ND	ND	323.15	ND	6.79	14.58	219.00	0.42	6.60	22.64	1.81
	B	7.89	-79	29.8	5.01	65.1	31.9	218	0.00	ND	289.86	ND	5.40	11.27	172.00	1.55	1.30	38.40	10.88
9	S	7.84	165	29.7	8.26	107.3	28.8	92	0.00	1.68	320.68	ND	4.68	27.70	223.00	0.71	0.00	31.50	4.96
	B	7.99	-25	29.7	7.73	100.4	31.9	134	0.00	ND	682.22	0.13	2.95	7.25	515.00	0.51	88.20	40.42	0.87
10	S	7.66	158	29.7	8.64	112.2	29.5	130	ND	ND	292.92	0.36	3.75	6.82	209.00	0.62	0.00	30.10	1.94
	B	8.01	-28	29.7	7.53	97.8	32.0	140	0.00	ND	209.10	0.07	3.19	6.59	156.00	0.64	92.60	39.26	14.98
11	S	7.92	207	29.6	8.18	105.5	30.0	105	ND	ND	201.06	0.07	3.15	2.11	147.00	0.76	8.90	42.46	6.11
	B	8.29	-72	29.3	4.09	52.4	34.4	102	ND	ND	310.49	0.06	2.90	8.25	188.00	0.51	104.50	37.40	1.30
12	S	7.66	193	29.6	9.23	119.1	29.9	108	0.00	ND	176.33	0.04	3.87	9.63	132.00	0.38	12.70	35.76	5.42
	B	8.30	-40	28.8	0.78	10.0	31.6	107	0.00	ND	181.40	0.04	2.60	8.09	126.00	0.22	88.20	36.74	6.30

* S = Dissolved Sulfide / S. Solid = Suspended Solid
ND = Non Detectable

Table E-3. Analtyical Results of the Water in Autumn

Location	B/S	pH	Eh (mv)	Temp (°C)	DO (mg/l)	DO (%)	Sal. (ppt)	S. Solid * (mg/l)	S * (mg/l)	TOC (mg/l)	labile Metals (μg/l)				Total Metals (μg/l)				
											Zn	Cd	Pb	Cu	Zn	Cd	Pb	Cu	Ni
1	S	7.10	167	25.5	2.6	31.3	2.2	295	0.01	2.25	183.66	ND	11.77	27.16	172.00	0.13	24.50	7.66	17.00
	B	7.45	-340	28.0	0.23	2.9	24.6	334	0.16	ND	220.10	ND	9.24	ND	185.00	0.67	59.40	26.48	2.40
2	S	7.51	20	25.7	5.22	63.7	4.9	377	0.01	2.37	256.57	0.14	7.19	9.11	254.00	0.18	14.70	18.78	1.20
	B	7.66	-322	27.8	0.37	4.7	22.7	385	0.07	ND	261.40	0.05	5.81	3.22	198.00	0.12	0.00	26.94	1.64
3	S	7.51	-44	25.9	4.04	49.3	4.5	214	0.01	3.43	326.58	0.14	3.72	4.01	269.00	0.68	19.10	8.72	2.69
	B	7.53	-34	27.3	0.89	11.1	14.7	170	0.01	4.66	409.17	0.22	6.08	9.22	299.00	0.12	6.60	10.44	1.32
4	S	7.64	9	26.0	5.35	65.2	5.1	164	0.01	2.50	239.69	0.72	5.88	2.32	236.00	0.31	83.30	13.86	7.04
	B	7.55	-6	27.9	0.81	9.1	19.4	211	0.01	ND	205.43	ND	8.40	9.07	165.00	0.67	43.00	14.42	11.26
5	S	8.41	5	26.3	9.09	110.9	10.2	187	0.01	3.63	233.45	0.10	4.83	4.30	221.00	0.53	16.30	12.24	1.77
	B	7.88	7	27.2	4.25	52.5	16.0	159	0.01	2.69	196.82	ND	4.92	50.43	171.00	0.47	41.20	15.10	2.03
6	S	8.52	21	27.1	10.00	123.6	11.5	159	0.03	3.47	284.11	ND	4.47	3.88	267.00	0.66	25.50	14.40	3.47
	B	7.82	13	27.7	0.36	4.5	27.8	213	0.01	ND	261.05	ND	5.06	12.53	189.00	0.26	68.10	36.70	10.12
7	S	8.45	28	26.6	11.30	138.4	12.6	170	0.01	3.56	183.97	ND	5.02	3.40	153.00	0.32	33.50	19.96	5.82
	B	7.89	22	27.5	1.03	12.9	29.0	116	0.01	ND	366.24	ND	3.84	2.44	284.00	0.26	39.90	28.50	7.72
8	S	8.26	46	26.8	8.16	100.7	10.7	138	0.00	1.88	193.73	ND	6.15	3.86	224.00	0.45	0.00	14.70	4.78
	B	7.75	42	27.7	1.35	17.1	24.9	10	0.01	ND	164.73	ND	4.51	2.80	161.00	0.16	24.60	26.94	6.21
9	S	8.75	19	27.0	12.70	156.5	12.2	153	0.01	3.40	441.97	ND	4.74	2.56	409.00	0.02	5.70	11.64	1.78
	B	7.86	25	27.5	1.29	16.1	28.4	105	0.01	3.63	850.29	ND	3.70	1.93	704.00	0.10	88.20	26.04	16.83
10	S	8.45	23	27.1	12.60	155.8	13.2	110	ND	3.90	191.67	2.56	4.01	3.45	127.00	0.11	6.60	15.46	4.52
	B	7.87	11	27.5	1.15	14.4	30.4	113	0.00	4.58	382.97	0.06	3.42	1.83	330.00	0.09	92.60	25.08	10.96
11	S	8.79	27	27.3	13.30	166.1	14.0	175	0.00	4.47	246.25	0.11	4.18	3.33	200.00	0.59	21.10	13.38	4.43
	B	7.89	25	27.5	1.56	19.5	30.2	105	0.14	3.71	347.38	ND	3.89	2.12	302.00	0.40	1.90	27.72	3.71
12	S	8.93	23	27.7	13.60	172.5	14.3	170	0.00	3.17	421.79	ND	4.11	4.51	342.00	0.27	21.10	14.26	10.24
	B	7.95	2	27.4	2.18	27.3	28.5	67	0.01	0.00	209.66	0.08	4.43	5.46	187.00	1.84	6.60	30.46	9.19

* S = Dissolved Sulfide / S. Solid = Suspended Solid
ND = Non Detectable

Table E-4. Analtyical Results of the Water in Winter

Location	B/S	pH	Eh (mv)	Temp (°C)	DO (mg/l)	DO (%)	Sal. (ppt)	S. Solid * (mg/l)	S * (mg/l)	TOC (mg/l)	labile Metals (μg/l)				Total Metals (μg/l)				
											Zn	Cd	Pb	Cu	Zn	Cd	Pb	Cu	Ni
1	S	7.12	61	17.6	0.58	6.0	15.1	249	0.01	4.44	620.99	2.88	3.71	3.03	602.00	3.73	20.60	16.92	19.71
	B	7.73	-273	20.3	0.22	2.4	24.6	233	0.02	ND	570.94	0.04	3.29	2.04	491.00	1.94	12.60	35.10	9.46
2	S	7.96	-131	17.7	2.20	22.9	20.4	295	0.02	5.32	372.58	ND	4.43	2.70	335.00	1.96	6.10	21.66	14.65
	B	7.86	-56	20.5	0.46	5.1	24.9	303	0.02	ND	416.76	0.14	2.36	1.62	354.00	1.75	5.70	28.92	7.72
3	S	7.54	-218	19.3	1.16	12.5	24.0	390	0.05	4.85	295.42	ND	2.69	2.65	267.00	1.78	13.60	26.70	8.89
	B	7.70	-79	20.3	0.37	4.8	28.5	299	0.01	ND	357.83	0.11	2.78	1.96	308.00	1.81	20.60	41.62	8.37
4	S	8.25	-51	18.4	3.97	42.2	23.8	744	0.02	4.70	345.51	0.36	3.48	4.30	287.00	3.18	8.40	24.24	8.57
	B	7.95	-47	20.1	1.28	13.9	23.8	298	0.01	ND	329.23	0.32	3.14	2.69	293.00	3.49	16.40	26.72	4.56
5	S	8.24	-23	18.2	3.61	38.0	24.1	341	0.04	5.73	525.71	0.16	2.70	3.54	442.00	1.95	21.90	17.32	13.15
	B	8.04	-24	20.1	1.37	14.9	31.1	245	0.03	ND	407.48	0.11	2.67	2.78	334.00	2.21	18.90	35.40	38.17
6	S	8.31	-10	18.5	3.85	41.0	26.6	311	0.00	4.44	985.10	0.60	2.93	2.53	991.00	2.38	47.90	18.30	15.11
	B	8.06	-55	19.6	1.61	17.4	30.7	223	0.04	ND	227.19	0.42	2.60	2.54	191.00	2.71	39.70	30.76	13.08
7	S	8.37	-7	18.7	4.04	43.0	28.8	185	0.04	4.53	201.74	0.24	2.51	2.68	186.00	1.42	23.50	24.88	8.57
	B	8.17	-5	19.2	2.34	25.2	31.5	152	0.02	ND	216.26	0.28	2.49	2.53	194.00	1.91	31.20	28.96	8.07
8	S	8.31	-5	19.2	4.40	47.3	28.8	521	0.03	6.05	233.22	0.24	3.59	ND	223.00	1.39	31.40	26.10	6.69
	B	8.18	-1	19.4	2.33	25.2	30.9	29	0.02	ND	204.80	0.14	2.75	3.30	181.00	1.50	31.10	23.58	11.39
9	S	8.23	3	19.2	3.33	35.8	29.1	108	0.01	10.81	244.52	0.72	3.24	3.06	201.00	0.92	42.90	31.66	14.84
	B	8.23	3	19.2	2.52	27.1	31.1	16	0.01	ND	207.84	0.05	2.68	2.76	186.00	0.21	45.5	28.56	10.72
10	S	8.30	9	19.2	3.48	37.4	30.1	100	0.01	ND	198.43	ND	2.77	2.27	180.00	0.04	130	28.36	12.09
	B	8.25	-1	19.2	2.04	21.9	31.7	27	0.01	ND	283.58	0.12	2.58	2.75	173.00	0.35	2.20	33.18	23.36
11	S	8.37	11	19.2	3.21	34.5	30.7	31	0.03	ND	440.92	0.11	3.06	2.96	374.00	3.18	4.20	28.02	27.78
	B	8.17	-31	19.6	1.61	17.4	31.6	30	0.02	ND	297.31	0.08	2.77	2.26	256.00	0.27	4.90	35.52	14.45
12	S	8.41	7	19.2	3.52	37.8	30.9	21	0.01	ND	180.56	0.04	2.58	2.96	168.00	0.17	0.00	36.64	12.96
	B	8.06	-13	19.5	0.88	9.7	33.2	12	0.02	ND	188.12	0.13	2.47	2.83	173.00	0.21	33.00	46.86	18.47

* S = Dissolved Sulfide / S. Solid = Suspended Solid
ND = Non Detectable

Appendix F. Analytical Results of the Bottom Sediments

Table F-1. Analytical Results of the Sediments in Spring

Location	pH	Eh (mv)	Temp. (°C)	AVS (μmol/g)	TC (%)	Simultaneously Extracted Metals (μmol/g)					SEM/AVS molar ratio	Grain Size (% < 63 μm)
						Zn	Cd	Pb	Cu	Ni		
1	7.06	-357	17.0	140.53	7.49	4.06	0.03	0.51	0.09	0.25	0.035	82.0
2	7.67	-342	17.0	140.42	23.53	4.88	0.04	0.55	0.22	0.37	0.043	90.2
3	6.95	-339	17.5	190.76	17.44	15.08	0.06	1.27	0.15	1.49	0.095	70.7
4	7.90	-218	18.0	60.83	3.87	3.58	0.01	0.20	0.07	0.17	0.066	87.5
5	7.70	-288	18.0	47.81	4.55	2.46	0.01	0.38	0.07	0.14	0.064	81.0
6	7.66	-276	18.0	92.64	17.08	3.24	0.02	0.37	0.15	0.22	0.043	90.6
7	7.75	-304	19.0	53.76	8.11	2.49	0.01	0.36	0.21	0.14	0.060	82.6
8	7.21	-28	18.0	3.51	0.44	0.68	0.00	0.09	0.10	0.05	0.266	5.1
9	7.28	-69	18.0	0.79	0.92	0.32	0.00	0.05	0.06	0.02	0.580	17.4
10	7.66	-80	18.5	26.14	5.26	1.18	0.01	0.21	0.15	0.07	0.062	25.3
11	7.26	-393	18.0	170.70	9.52	10.37	0.09	1.27	2.11	1.08	0.087	89.8
12	7.55	-319	19.0	65.41	13.33	1.76	0.01	0.28	0.29	0.12	0.038	69.6

Table F-2. Analytical Results of the Sediments in Summer

Location	pH	Eh (mv)	Temp. (°C)	AVS (μmol/g)	TC (%)	Simultaneously Extracted Metals (μmol/g)					SEM/AVS molar ratio	Grain Size (% < 63 μm)
						Zn	Cd	Pb	Cu	Ni		
1	7.00	-393	28.9	214.49	26.12	7.01	0.01	0.63	0.02	0.19	0.037	76.0
2	7.43	-376	28.7	145.11	5.32	5.31	0.01	0.50	0.16	0.15	0.042	79.2
3	7.23	-396	29.2	135.99	4.62	7.11	0.00	0.54	0.02	0.22	0.058	28.7
4	7.84	-382	29.3	124.82	2.83	3.24	0.00	0.32	0.19	0.10	0.031	85.1
5	7.64	-330	29.2	87.70	11.10	4.12	0.01	0.44	0.09	0.10	0.054	86.8
6	7.73	-373	29.2	58.89	3.93	2.77	0.01	0.38	0.20	0.08	0.058	92.0
7	7.74	-368	29.2	66.19	2.54	2.69	0.00	0.31	0.22	0.08	0.050	80.9
8	8.10	-84	30.0	10.64	0.61	0.62	0.00	0.08	0.03	0.01	0.070	4.9
9	7.78	-326	29.8	33.27	2.22	1.16	0.00	0.17	0.12	0.03	0.044	38.4
10	7.80	-342	29.8	44.65	1.54	2.21	0.00	0.25	0.16	0.05	0.060	65.6
11	7.42	-402	28.2	252.49	3.14	4.69	0.01	0.38	0.93	0.21	0.025	81.9
12	7.68	-344	31.2	87.98	5.44	2.37	0.00	0.27	0.23	0.09	0.034	63.6

Table F-3. Analytical Results of the Sediments in Autumn

Location	pH	Eh (mv)	Temp. (°C)	AVS (μmol/g)	TC (%)	Simultaneously Extracted Metals (μmol/g)					SEM/AVS molar ratio	Grain Size (% < 63 μm)
						Zn	Cd	Pb	Cu	Ni		
1	7.27	-449	28.0	80.71	1.95	4.84	0.00	0.57	0.07	0.11	0.069	39.0
2	8.57	-419	27.8	135.19	5.39	5.06	0.01	0.55	0.10	0.16	0.043	88.7
3	7.65	-337	28.4	43.07	1.14	2.60	0.00	0.15	0.01	0.09	0.066	14.1
4	7.71	-264	27.3	26.94	0.87	0.98	0.00	0.12	0.04	0.03	0.044	93.3
5	7.64	-375	27.5	66.51	5.59	3.07	0.00	0.34	0.13	0.08	0.054	73.8
6	7.91	-337	28.9	55.70	3.88	2.86	0.00	0.40	0.29	0.12	0.066	87.9
7	7.92	-377	28.2	102.89	3.39	2.62	0.00	0.32	0.19	0.08	0.031	85.0
8	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------
9	8.15	-336	28.6	25.08	1.54	1.22	0.00	0.14	0.08	0.03	0.059	29.0
10	8.14	-189	28.5	3.89	2.90	0.40	0.00	0.08	0.07	0.01	0.144	29.2
11	8.03	-239	27.4	1.76	2.15	0.90	0.00	0.18	0.08	0.01	0.666	48.8
12	7.67	-383	17.4	26.59	5.85	1.04	0.00	0.13	0.11	0.03	0.049	55.1

Table F-4. Analytical Results of the Sediments in Winter

Location	pH	Eh (mv)	Temp. (°C)	AVS (μmol/g)	TC (%)	Simultaneously Extracted Metals (μmol/g)					SEM/AVS molar ratio	Grain Size (% < 63 μm)
						Zn	Cd	Pb	Cu	Ni		
1	7.63	-394	20.3	220.52	4.59	5.06	0.00	0.55	0.00	0.12	0.026	82.2
2	7.65	-404	20.3	125.67	6.93	5.86	0.01	0.55	0.08	0.16	0.053	92.3
3	7.89	-389	20.2	58.67	1.52	2.91	0.00	0.16	0.00	0.15	0.055	13.6
4	7.94	-289	20.1	18.24	0.80	1.37	0.00	0.08	0.07	0.04	0.086	84.0
5	7.24	-390	20.1	191.51	5.19	4.47	0.01	0.40	0.03	0.10	0.026	87.5
6	7.97	-262	19.6	39.98	6.05	1.92	0.00	0.25	0.24	0.09	0.063	71.6
7	7.65	-344	19.2	124.44	11.97	3.10	0.00	0.31	0.15	0.10	0.029	76.8
8	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------
9	7.78	-260	19.2	12.01	1.31	0.60	0.00	0.07	0.05	0.02	0.061	19.6
10	--------	--------	--------	12.01	--------	0.43	0.00	0.04	0.02	0.02	0.042	--------
11	7.90	-380	19.6	9.64	2.01	0.79	0.00	0.09	0.06	0.02	0.099	38.3
12	7.73	-369	19.5	18.12	1.53	1.48	0.00	0.22	0.21	0.03	0.107	54.1

Appendix G. Analytical Results of the Pore Water

Table G-1. Analytical Results of the Pore Water in Spring

Location	pH	Eh (mv)	Temp (°C)	Sal. (ppt)	S (mg/l)	TOC (mg/l)	Labile Metals (μg/l)				Total Metals (μg/l)				
							Zn	Cd	Pb	Cu	Zn	Cd	Pb	Cu	Ni
1	8.23	-182	18.1	29.4	0.14	10.10	181.99	0.15	5.21	3.16	199.00	0.32	41.00	69.34	2.55
2	8.61	53	18.1	28.3	0.00	0.00	249.28	0.28	7.44	7.84	287.00	1.98	43.00	32.82	ND
3	8.51	-137	18.1	27.5	0.10	9.20	271.77	0.27	15.50	10.10	325.00	1.91	50.00	54.34	2.26
4	8.86	-53	18.1	27.8	0.00	9.50	185.33	0.33	11.30	12.97	216.00	3.18	77.00	53.72	ND
5	8.77	1	18.1	31.3	0.00	9.50	242.52	0.67	26.72	38.10	299.00	3.49	64.00	64.16	ND
6	8.87	16	18.1	29.4	0.01	15.80	181.30	0.00	14.13	ND	266.00	4.09	38.00	68.00	ND
7	8.87	22	18.1	31.2	0.00	13.60	249.13	0.07	9.17	8.04	335.00	4.82	14.00	76.90	ND
8	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------
9	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------
10	8.69	14	18.1	30.2	0.00	172.80	419.58	ND	15.04	15.58	448.00	4.45	24.00	79.50	130.10
11	8.98	-399	18.1	31.9	180.36	21.60	20.26	6.89	3.45	6.29	174.00	2.86	20.00	75.90	0.92
12	8.78	-193	18.1	33.0	0.06	13.40	318.17	0.66	198.46	49.06	307.00	6.31	42.00	77.40	ND

*ND = nondetectable

Table G-2. Analytical Results of the Pore Water in Summer

Location	pH	Eh (mv)	Temp (°C)	Sal. (ppt)	S (mg/l)	TOC (mg/l)	Labile Metals (μg/l)				Total Metals (μg/l)				
							Zn	Cd	Pb	Cu	Zn	Cd	Pb	Cu	Ni
1	7.26	-380	18.5	24.2	57.64	25.70	191.90	ND	ND	ND	110.00	1.12	0.00	72.30	3.64
2	7.69	-317	18.5	25.3	4.80	11.60	329.10	0.52	48.98	ND	213.00	0.38	31.70	72.80	0.84
3	7.50	-372	18.5	23.9	32.28	17.30	249.00	6.93	679.94	ND	174.00	0.75	21.4	74.30	1.86
4	7.80	-308	18.5	35.7	5.09	10.20	127.10	ND	3.07	ND	81.00	0.01	6.90	71.50	ND
5	7.38	-117	18.5	36.3	0.05	0.00	204.22	ND	8.72	2.60	105.00	1.68	21.40	79.50	6.09
6	7.49	-87	18.5	36.0	0.04	9.80	303.68	ND	6.29	2.25	200.00	0.33	6.90	75.30	12.90
7	7.59	-208	18.5	36.4	0.33	10.80	173.72	ND	17.76	ND	101.00	0.02	21.40	79.90	25.24
8	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------
9	7.47	-82	18.5	36.0	0.03	13.70	277.91	0.54	12.36	2.33	175.00	ND	0.00	73.50	ND
10	7.53	-63	18.5	35.9	0.03	21.30	240.16	ND	5.67	10.36	223.00	0.95	31.70	78.70	2.39
11	7.47	-401	18.5	36.6	128.79	14.50	ND	ND	2754.90	ND	74.00	0.76	32.30	81.30	16.05
12	7.74	-345	18.5	37.2	28.90	0.00	258.18	ND	ND	46.57	142.00	0.34	31.90	75.10	2.77

*ND = Non Detectable

Table G-3. Analytical Results of the Pore Water in Autumn

Location	pH	Eh (mv)	Temp (°C)	Sal. (ppt)	S (mg/l)	TOC (mg/l)	Labile Metals (μg/l)				Total Metals (μg/l)				
							Zn	Cd	Pb	Cu	Zn	Cd	Pb	Cu	Ni
1	7.70	-402	17.0	27.2	57.33	18.80	126.23	0.42	5.67	ND	360.00	ND	0.00	61.5	10.96
2	7.85	-401	17.0	28.3	45.55	9.70	48.76	ND	4.93	ND	122.00	2.20	0.00	87.7	2.83
3	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------
4	8.00	-168	17.0	26.9	0.05	8.00	291.29	ND	7.05	3.01	191.00	1.20	0.00	43.9	ND
5	8.01	-249	17.0	28.1	2.53	8.20	314.99	ND	8.25	3.04	246.00	1.11	0.00	54.4	0.44
6	8.07	-190	17.1	28.7	0.10	6.70	159.70	0.60	4.13	ND	115.00	0.76	0.00	69.2	22.87
7	7.90	-233	17.1	30.8	2.15	8.20	164.32	0.42	4.03	1.41	121.00	0.80	0.00	68.2	ND
8	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------
9	8.04	-120	17.2	28.4	0.04	30.70	1347.30	ND	3.98	3.10	1191.00	0.59	67.80	48.0	ND
10	8.08	-94	17.2	26.6	0.06	-------	-------	-------	-------	-------	4956.00	0.16	113.90	42.2	6.30
11	7.95	-74	17.2	30.3	0.04	4.30	549.05	ND	4.59	10.12	421.00	0.34	21.40	58.6	2.16
12	7.93	-323	17.2	31.3	15.20	4.60	387.91	0.78	2.63	ND	277.00	0.32	21.40	68.0	ND

*ND = Non Detectable

Table G-4. Analytical Results of the Pore Water in Winter

Location	pH	Eh	Temp	Sal.	S	TOC	Labile Metals (μg/l)				Total Metals (μg/l)				
		(mv)	(°C)	(ppt)	(mg/l)	(mg/l)	Zn	Cd	Pb	Cu	Zn	Cd	Pb	Cu	Ni
1	7.89	-362	13.3	28.8	33.46	9.73	215.79	ND	3.74	1.50	155.00	1.85	83.50	152.40	4.49
2	8.15	-299	14.4	28.3	13.08	6.20	278.56	ND	109.61	ND	200.00	1.02	26.00	151.40	1.22
3	8.3	-67.2	16.2	28.4	-------	13.1	-------	-------	-------	-------	-------	-------	-------	-------	-------
4	8.20	-85	16.4	28.2	0.20	12.40	459.46	ND	3.81	0.00	372.00	0.27	103.10	136.8	1.37
5	8.00	-300	16.6	29.6	26.29	0.00	537.47	ND	6.16	0.98	431.00	0.45	96.70	160.8	5.39
6	8.17	-93	16.8	30.3	0.14	6.12	528.95	ND	3.30	4.30	434.00	0.45	58.10	110.0	ND
7	8.07	-147	16.9	29.6	1.07	0.00	225.54	ND	6.98	ND	161.00	0.69	148.10	136.8	4.09
8	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------
9	8.03	-73	17.1	31.9	0.20	0.00	1208.80	42.30	3.09	1.78	1059.00	0.74	14.00	126.20	1.91
10	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------
11	8.26	-256	16.8	32.2	8.09	0.43	304.41	ND	6.15	ND	226.00	0.69	20.50	136.00	2.98
12	8.11	-259	16.6	32.5	7.56	10.00	226.68	ND	6.92	ND	156.00	0.63	14.60	145.40	3.84

* ND = Non Detectable

Appendix H. Concentrations (μg/g) and Fractions (%) of Pb in Sediments

Table H-1. Concentrations (μg/g) and Fractions (%) of Pb in Sediments (Spring)

point	Pb (μg/g)						% of Total				
	I	II	III	IV	V	Total	I	II	III	IV	V
1	0.02	12.60	40.55	6.03	53.76	112.97	0.0	11.2	35.9	5.3	47.6
2	0.01	15.62	37.10	3.35	46.72	102.80	0.0	15.2	36.1	3.3	45.4
3	0.09	22.18	27.01	12.48	109.25	171.00	0.0	13.0	15.8	7.3	63.9
4	0.03	3.47	13.15	1.00	23.11	40.76	0.0	8.5	32.2	2.5	56.7
5	0.02	12.64	28.46	6.40	39.77	87.29	0.0	14.5	32.6	7.3	45.6
6	0.01	10.35	29.87	4.35	45.73	90.31	0.0	11.5	33.1	4.8	50.6
7	0.01	12.17	25.31	8.49	39.44	85.42	0.0	14.2	29.6	9.9	46.2
8	0.00	2.33	7.38	0.52	12.84	23.08	0.0	10.1	32.0	2.3	55.6
9	0.00	1.14	4.94	0.05	11.68	17.82	0.0	6.4	27.7	0.3	65.6
10	0.00	1.65	14.55	1.66	24.31	42.18	0.0	3.9	34.5	3.9	57.6
11	0.02	11.90	21.20	3.13	43.10	79.34	0.0	15.0	26.7	3.9	54.3
12	0.03	10.94	18.67	4.38	35.74	69.75	0.0	15.7	26.8	6.3	51.2

Table H-2. Concentrations (μg/g) and Fractions (%) of Pb in Sediments (Summer)

point	Pb (μg/g)						% of Total				
	I	II	III	IV	V	Total	I	II	III	IV	V
1	0.06	18.70	46.58	5.70	51.22	122.26	0.0	15.3	38.1	4.7	41.9
2	0.03	25.49	36.92	3.21	38.23	103.89	0.0	24.5	35.5	3.1	36.8
3	0.08	8.20	62.75	8.31	52.80	132.14	0.0	6.2	47.5	6.3	40.0
4	0.14	15.16	25.16	2.53	32.03	75.02	0.2	20.2	33.5	3.4	42.7
5	0.05	19.42	32.61	8.38	44.78	105.25	0.0	18.5	31.0	8.0	42.5
6	0.01	20.68	28.75	0.21	53.07	102.71	0.0	20.1	28.0	0.2	51.7
7	0.00	14.46	22.44	6.56	37.96	81.44	0.0	17.8	27.6	8.1	46.6
8	0.02	4.25	9.11	0.24	8.93	22.55	0.0	18.8	40.4	1.1	39.6
9	0.00	5.81	14.77	3.41	27.16	51.17	0.0	11.4	28.9	6.7	53.1
10	0.00	11.92	17.74	3.13	38.03	70.83	0.0	16.8	25.0	4.4	53.7
11	0.05	17.24	21.56	3.18	38.77	80.81	0.0	21.3	26.7	3.9	48.0
12	0.02	14.56	19.18	4.49	34.06	72.30	0.0	20.1	26.5	6.2	47.1

Table H-3. Concentrations (μg/g) and Fractions (%) of Pb in Sediments (Autumn)

point	Pb (μg/g)						% of Total				
	I	II	III	IV	V	Total	I	II	III	IV	V
1	0.29	13.43	31.38	6.87	36.76	88.73	0.3	15.1	35.4	7.7	41.4
2	0.54	26.65	41.51	5.41	37.79	111.89	0.5	23.8	37.1	4.8	33.8
3	0.27	10.27	37.94	3.91	46.45	98.84	0.3	10.4	38.4	4.0	47.0
4	0.23	4.74	8.92	0.83	17.34	32.07	0.7	14.8	27.8	2.6	54.1
5	0.31	14.11	23.07	4.33	29.90	71.71	0.4	19.7	32.2	6.0	41.7
6	0.05	16.50	23.38	0.02	33.82	73.77	0.0	22.4	31.7	0.0	45.8
7	0.02	12.59	21.17	3.29	29.70	66.78	0.0	18.9	31.7	4.9	44.5
8	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
9	0.02	4.61	9.57	3.10	19.90	37.20	0.0	12.4	25.7	8.3	53.5
10	0.02	4.79	11.27	1.05	19.73	36.86	0.0	13.0	30.6	2.9	53.5
11	0.21	5.01	13.80	3.59	27.75	50.36	0.4	9.9	27.4	7.1	55.1
12	0.06	7.80	11.19	3.04	16.97	39.06	0.2	20.0	28.7	7.8	43.4

Table H-4. Concentrations (μg/g) and Fractions (%) of Pb in Sediments (Winter)

point	Pb (μg/g)						% of Total				
	I	II	III	IV	V	Total	I	II	III	IV	V
1	0.02	22.42	40.26	5.15	38.11	105.96	0.0	21.2	38.0	4.9	36.0
2	0.04	25.73	37.21	4.36	36.62	103.97	0.0	24.7	35.8	4.2	35.2
3	0.04	10.31	20.83	5.06	19.44	55.67	0.0	18.5	37.4	9.1	34.9
4	0.03	3.16	6.35	0.70	12.14	22.39	0.1	14.1	28.4	3.1	54.2
5	0.01	13.56	31.17	7.66	36.34	88.74	0.0	15.3	35.1	8.6	41.0
6	0.06	20.02	20.17	0.18	29.33	69.76	0.0	28.7	28.9	0.3	42.0
7	0.12	15.50	22.55	0.11	36.52	74.80	0.2	20.7	30.2	0.1	48.8
8	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
9	0.06	4.31	6.42	0.50	13.80	25.09	0.3	17.2	25.6	2.0	55.0
10	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
11	0.01	5.64	8.99	0.15	26.21	41.00	0.0	13.8	21.9	0.4	63.9
12	0.00	13.35	11.36	0.21	30.94	55.87	0.0	23.9	20.3	0.4	55.4

Appendix I. Concentrations (μg/g) and Fractions (%) of Cu in Sediments

Table I-1. Concentrations (μg/g) and Fractions (%) of Cu in Sediments (Spring)

point	Cu (μg/g)						% of Total				
	I	II	III	IV	V	Total	I	II	III	IV	V
1	0.40	0.22	1.23	33.51	15.53	50.89	0.8	0.4	2.4	65.8	30.5
2	0.74	0.23	1.89	64.50	29.13	96.48	0.8	0.2	2.0	66.9	30.2
3	0.68	1.34	5.90	423.28	76.40	507.60	0.1	0.3	1.2	83.4	15.1
4	0.18	0.22	0.86	10.79	11.82	23.86	0.7	0.9	3.6	45.2	49.5
5	0.27	0.30	0.76	36.54	17.15	55.03	0.5	0.5	1.4	66.4	31.2
6	0.42	0.27	1.15	42.50	24.30	68.64	0.6	0.4	1.7	61.9	35.4
7	0.26	0.66	0.49	47.54	21.92	70.88	0.4	0.9	0.7	67.1	30.9
8	0.02	0.11	0.04	8.72	6.55	15.43	0.1	0.7	0.3	56.5	42.4
9	0.03	0.17	0.04	0.84	3.56	4.64	0.8	3.6	0.9	18.1	76.6
10	0.13	0.17	0.02	16.00	11.35	27.67	0.5	0.6	0.0	57.8	41.0
11	0.42	0.69	1.78	108.12	40.86	151.87	0.3	0.5	1.2	71.2	26.9
12	0.33	0.52	0.33	43.33	18.39	62.91	0.5	0.8	0.5	68.9	29.2

Table I-2. Concentrations (μg/g) and Fractions (%) of Cu in Sediments (Summer)

point	Cu (μg/g)						% of Total				
	I	II	III	IV	V	Total	I	II	III	IV	V
1	0.77	0.88	1.65	66.72	17.89	87.91	0.9	1.0	1.9	75.9	20.4
2	0.85	0.92	4.72	80.09	26.67	113.25	0.7	0.8	4.2	70.7	23.6
3	0.17	0.73	1.91	197.47	21.93	222.21	0.0	0.3	0.9	88.9	9.9
4	0.44	0.50	4.37	55.84	25.76	86.90	0.5	0.6	5.0	64.3	29.6
5	0.45	0.40	2.50	80.59	26.18	110.12	0.4	0.4	2.3	73.2	23.8
6	0.59	1.21	1.92	71.97	29.71	105.41	0.6	1.2	1.8	68.3	28.2
7	0.52	1.05	0.79	40.96	21.82	65.14	0.8	1.6	1.2	62.9	33.5
8	0.09	0.12	0.12	2.45	3.84	6.63	1.4	1.8	1.8	37.0	58.0
9	0.21	0.49	0.26	19.09	10.41	30.45	0.7	1.6	0.8	62.7	34.2
10	0.39	0.91	0.98	44.49	19.27	66.03	0.6	1.4	1.5	67.4	29.2
11	1.68	1.22	7.70	175.85	52.96	239.41	0.7	0.5	3.2	73.5	22.1
12	0.86	1.13	1.80	62.88	27.31	93.98	0.9	1.2	1.9	66.9	29.1

Table I-3. Concentrations (μg/g) and Fractions (%) of Cu in Sediments (Autumn)

point	Cu (μg/g)						% of Total				
	I	II	III	IV	V	Total	I	II	III	IV	V
1	0.25	0.44	0.39	26.79	5.69	33.57	0.8	1.3	1.2	79.8	17.0
2	0.36	1.17	4.90	92.99	22.32	121.73	0.3	1.0	4.0	76.4	18.3
3	0.11	0.16	1.73	99.87	7.79	109.65	0.0	0.1	1.6	91.1	7.1
4	0.11	0.57	1.54	4.81	5.69	12.73	0.9	4.5	12.1	37.8	44.7
5	0.28	0.44	1.97	59.08	11.95	73.72	0.4	0.6	2.7	80.1	16.2
6	0.32	0.58	3.08	59.19	17.34	80.51	0.4	0.7	3.8	73.5	21.5
7	0.41	0.53	1.22	45.40	15.20	62.76	0.7	0.8	1.9	72.3	24.2
8	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
9	0.06	0.21	0.15	12.37	6.15	18.94	0.3	1.1	0.8	65.3	32.5
10	0.09	0.37	0.49	11.85	5.10	17.90	0.5	2.1	2.7	66.2	28.5
11	0.31	0.70	0.05	5.82	6.53	13.41	2.3	5.2	0.4	43.4	48.7
12	0.60	0.51	0.87	18.66	6.05	26.69	2.2	1.9	3.3	69.9	22.7

Table I-4. Concentrations (μg/g) and Fractions (%) of Cu in Sediments (Winter)

point	Cu (μg/g)						% of Total				
	I	II	III	IV	V	Total	I	II	III	IV	V
1	1.41	1.76	0.79	45.36	11.00	60.32	2.3	2.9	1.3	75.2	18.2
2	0.67	1.61	1.95	73.08	15.35	92.66	0.7	1.7	2.1	78.9	16.6
3	0.25	0.27	0.28	73.95	11.37	86.12	0.3	0.3	0.3	85.9	13.2
4	0.54	0.92	0.00	6.59	7.81	15.86	3.4	5.8	0.0	41.5	49.2
5	0.71	8.52	0.00	60.99	12.85	83.08	0.9	10.3	0.0	73.4	15.5
6	0.72	7.86	0.00	85.73	15.38	109.69	0.7	7.2	0.0	78.2	14.0
7	0.50	0.78	0.00	43.01	11.70	55.99	0.9	1.4	0.0	76.8	20.9
8	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
9	0.33	0.23	0.07	5.72	3.93	10.28	3.3	2.2	0.7	55.6	38.2
10	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
11	0.41	0.25	0.09	13.81	4.49	19.05	2.2	1.3	0.5	72.5	23.6
12	0.87	1.30	0.17	26.25	7.62	36.21	2.4	3.6	0.5	72.5	21.0

Appendix J. Concentrations (μg/g) and Fractions (%) of Cd in Sediments

Table J-1. Concentrations (μg/g) and Fractions (%) of Cd in Sediments (Spring)

point	Cd (μg/g)						% of Total				
	I	II	III	IV	V	Total	I	II	III	IV	V
1	0.02	0.04	0.91	1.07	0.26	2.29	0.9	1.5	39.7	46.6	11.2
2	0.03	0.11	1.14	1.17	0.27	2.72	1.0	4.0	41.9	43.2	9.8
3	0.03	0.03	1.32	1.70	0.41	3.48	0.7	0.8	37.8	48.8	11.8
4	0.01	0.02	0.36	0.31	0.11	0.81	1.8	3.0	44.1	38.1	12.9
5	0.02	0.10	0.64	0.86	0.14	1.76	1.0	5.6	36.5	48.7	8.2
6	0.02	0.06	0.66	0.93	0.23	1.90	1.0	3.1	34.6	49.1	12.2
7	0.01	0.22	0.40	0.67	0.15	1.45	1.0	15.3	27.5	46.2	10.1
8	0.00	0.02	0.10	0.10	0.07	0.29	1.5	6.7	33.1	34.0	24.7
9	0.00	0.01	0.05	0.04	0.09	0.19	2.6	5.3	23.8	22.9	45.4
10	0.00	0.08	0.15	0.33	0.08	0.65	1.0	13.1	23.5	50.5	11.8
11	0.04	0.26	0.32	0.88	0.18	1.67	2.2	15.7	19.0	52.6	10.6
12	0.03	0.25	0.16	0.52	0.09	1.05	2.6	23.6	15.7	49.8	8.3

Table J-2. Concentrations (μg/g) and Fractions (%) of Cd in Sediments (Summer)

point	Cd (μg/g)						% of Total				
	I	II	III	IV	V	Total	I	II	III	IV	V
1	0.04	0.06	1.69	1.05	1.00	3.84	1.1	1.5	44.0	27.3	26.1
2	0.00	0.29	1.53	0.79	1.10	3.71	0.2	7.8	41.2	21.4	29.5
3	0.01	0.02	0.76	0.60	0.40	1.79	0.7	1.0	42.7	33.5	22.1
4	0.02	0.09	0.96	0.47	0.65	2.19	1.1	4.2	43.6	21.6	29.4
5	0.02	0.13	1.10	0.49	0.65	2.38	0.8	5.4	46.1	20.5	27.1
6	0.02	0.22	0.82	0.62	0.63	2.31	0.9	9.7	35.5	26.7	27.2
7	0.02	0.22	0.73	0.31	0.55	1.84	1.0	12.0	39.8	17.1	30.1
8	0.00	0.02	0.21	0.03	0.25	0.52	1.2	3.2	41.1	6.7	47.8
9	0.01	0.08	0.35	0.19	0.32	0.95	1.3	8.6	36.9	19.6	33.5
10	0.02	0.21	0.54	0.24	0.52	1.53	1.1	13.9	35.4	15.6	33.9
11	0.05	0.31	1.07	0.51	1.17	3.11	1.7	10.1	34.4	16.3	37.6
12	0.03	0.27	0.58	0.28	0.76	1.92	1.6	14.2	30.2	14.6	39.3

Table J-3. Concentrations (μg/g) and Fractions (%) of Cd in Sediments (Autumn)

point	Cd (μg/g)						% of Total				
	I	II	III	IV	V	Total	I	II	III	IV	V
1	0.01	0.04	0.47	0.23	0.09	0.84	1.4	5.1	55.7	26.8	11.0
2	0.03	0.06	1.01	0.43	0.13	1.66	1.8	3.7	60.8	25.7	7.9
3	0.00	0.00	0.36	0.11	0.08	0.55	1.4	0.3	64.1	19.3	15.0
4	0.02	0.00	0.22	0.09	0.07	0.40	3.8	0.9	54.1	22.6	18.6
5	0.02	0.14	0.63	0.20	0.09	1.08	1.9	12.8	58.1	18.7	8.4
6	0.02	0.36	0.52	0.16	0.06	1.11	1.4	32.2	46.7	14.0	5.8
7	0.03	0.16	0.61	0.17	0.08	1.05	2.9	15.3	58.2	15.8	7.9
8	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
9	0.01	0.05	0.21	0.08	0.04	0.39	3.8	13.6	52.4	20.3	9.9
10	0.01	0.04	0.05	0.02	0.02	0.15	7.7	28.5	33.3	14.6	15.8
11	0.01	0.04	0.07	0.05	0.05	0.22	6.1	16.3	32.6	23.9	21.1
12	0.02	0.23	0.12	0.06	0.04	0.46	4.0	49.1	25.3	13.0	8.6

Table J-4. Concentrations (μg/g) and Fractions (%) of Cd in Sediments (Winter)

point	Cd (μg/g)						% of Total				
	I	II	III	IV	V	Total	I	II	III	IV	V
1	0.03	0.06	0.80	0.51	0.61	2.01	1.6	3.1	39.7	25.3	30.3
2	0.04	0.08	1.00	0.45	0.86	2.42	1.6	3.3	41.1	18.4	35.5
3	0.00	0.01	0.18	0.12	0.18	0.50	1.0	2.4	36.5	23.8	36.2
4	0.02	0.03	0.16	0.06	0.31	0.58	2.7	5.1	28.0	10.3	53.9
5	0.02	0.05	0.81	0.41	0.44	1.72	1.2	2.9	46.8	23.6	25.5
6	0.02	0.19	0.35	0.22	0.44	1.22	1.9	15.5	28.5	18.3	35.8
7	0.02	0.04	0.63	0.46	0.44	1.60	1.4	2.5	39.3	29.1	27.7
8	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
9	0.01	0.03	0.12	0.06	0.09	0.31	3.5	8.3	38.3	20.6	29.3
10	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
11	0.01	0.05	0.09	0.16	0.16	0.48	2.2	10.9	19.3	34.1	33.5
12	0.01	0.14	0.14	0.15	0.14	0.59	2.3	24.0	24.5	25.0	24.2

Appendix K. Concentrations (μg/g) and Fractions (%) of Zn in Sediments

Table K-1. Concentrations (μg/g) and Fractions (%) of Zn in Sediments (Spring)

point	Zn (μg/g)						% of Total				
	I	II	III	IV	V	Total	I	II	III	IV	V
1	0.25	20.28	157.43	98.28	53.76	330.00	0.0	6.1	47.7	29.8	16.3
2	0.13	42.49	147.81	103.48	46.72	340.62	0.0	12.5	43.4	30.4	13.7
3	1.16	52.88	551.76	385.44	109.25	1100.48	0.1	4.8	50.1	35.0	9.9
4	0.32	13.15	82.53	28.48	23.11	147.59	0.2	8.9	55.9	19.3	15.7
5	0.39	24.75	110.89	49.75	39.77	225.55	0.2	11.0	49.2	22.1	17.6
6	0.51	20.51	103.97	41.99	45.73	212.71	0.2	9.6	48.9	19.7	21.5
7	0.26	30.54	72.79	36.84	39.44	179.87	0.1	17.0	40.5	20.5	21.9
8	0.11	4.47	10.09	3.62	12.84	31.12	0.4	14.3	32.4	11.6	41.3
9	0.06	1.89	7.08	1.75	11.68	22.46	0.3	8.4	31.5	7.8	52.0
10	0.23	6.68	23.07	15.20	24.31	69.49	0.3	9.6	33.2	21.9	35.0
11	0.45	17.92	52.79	63.99	43.10	178.25	0.3	10.1	29.6	35.9	24.2
12	0.37	17.24	36.32	34.28	35.74	123.96	0.3	13.9	29.3	27.7	28.8

Table K-2. Concentrations (μg/g) and Fractions (%) of Zn in Sediments (Summer)

point	Zn (μg/g)						% of Total				
	I	II	III	IV	V	Total	I	II	III	IV	V
1	0.15	59.44	231.55	102.35	132.53	526.02	0.0	11.3	44.0	19.5	25.2
2	0.33	77.40	143.50	64.78	80.06	366.06	0.0	21.1	39.2	17.7	21.9
3	0.24	47.35	275.10	96.02	69.98	488.69	0.0	9.7	56.3	19.6	14.3
4	0.35	37.44	80.52	45.62	82.94	246.87	0.1	15.2	32.6	18.5	33.6
5	0.10	54.68	103.62	53.84	88.94	301.19	0.0	18.2	34.4	17.9	29.5
6	0.10	43.01	75.37	44.26	100.00	262.73	0.0	16.4	28.7	16.8	38.1
7	0.20	42.22	65.31	39.66	99.64	247.02	0.0	17.1	26.4	16.1	40.3
8	0.16	6.18	16.51	6.02	42.99	71.85	0.2	8.6	23.0	8.4	59.8
9	0.12	11.76	28.81	20.99	67.84	129.52	0.0	9.1	22.2	16.2	52.4
10	0.08	29.41	47.42	31.38	81.16	189.44	0.0	15.5	25.0	16.6	42.8
11	0.37	52.48	90.15	65.47	99.85	308.32	0.1	17.0	29.2	21.2	32.4
12	0.37	30.23	54.13	33.77	91.67	210.16	0.2	14.4	25.8	16.1	43.6

Table K-3. Concentrations (μg/g) and Fractions (%) of Zn in Sediments (Autumn)

point	Zn (μg/g)						% of Total				
	I	II	III	IV	V	Total	I	II	III	IV	V
1	0.15	20.78	110.48	50.70	49.73	231.83	0.0	9.0	47.7	21.9	21.4
2	0.16	55.32	200.73	88.51	73.18	417.90	0.0	13.2	48.0	21.2	17.5
3	0.10	21.36	111.07	33.66	74.77	240.97	0.0	8.9	46.1	14.0	31.0
4	0.25	10.92	31.02	12.09	70.87	125.15	0.2	8.7	24.8	9.7	56.6
5	0.21	36.08	94.92	49.20	62.11	242.53	0.0	14.9	39.1	20.3	25.6
6	0.10	32.18	71.32	40.43	64.96	208.98	0.0	15.4	34.1	19.3	31.1
7	0.22	31.23	68.66	36.45	74.86	211.42	0.1	14.8	32.5	17.2	35.4
8	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
9	0.07	10.10	27.35	18.19	46.00	101.70	0.0	9.9	26.9	17.9	45.2
10	0.05	3.39	10.26	6.24	31.74	51.68	0.0	6.6	19.9	12.1	61.4
11	0.36	0.97	21.99	8.64	76.95	108.90	0.3	0.9	20.2	7.9	70.7
12	0.09	15.49	37.99	16.26	38.08	107.91	0.0	14.4	35.2	15.1	35.3

Table K-4. Concentrations (μg/g) and Fractions (%) of Zn in Sediments (Winter)

point	Zn (μg/g)						% of Total				
	I	II	III	IV	V	Total	I	II	III	IV	V
1	0.62	31.75	187.68	61.62	61.78	343.45	0.2	9.2	54.6	17.9	18.0
2	0.82	39.76	157.00	60.35	66.47	324.40	0.3	12.3	48.4	18.6	20.5
3	0.19	19.70	69.08	16.70	14.87	120.55	0.2	16.3	57.3	13.9	12.3
4	0.59	9.26	26.09	10.86	63.04	109.83	0.5	8.4	23.8	9.9	57.4
5	0.59	37.93	160.10	65.50	61.97	326.09	0.2	11.6	49.1	20.1	19.0
6	0.48	28.60	67.86	37.22	58.16	192.33	0.2	14.9	35.3	19.4	30.2
7	0.25	37.02	85.71	39.48	69.11	231.57	0.1	16.0	37.0	17.0	29.8
8	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
9	0.26	5.98	18.00	10.46	33.60	68.30	0.4	8.8	26.4	15.3	49.2
10	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
11	0.28	4.23	21.34	15.17	44.42	85.44	0.3	4.9	25.0	17.8	52.0
12	0.37	14.33	28.57	19.62	50.29	113.17	0.3	12.7	25.2	17.3	44.4

Appendix L. Concentrations (μg/g) and Fractions (%) of Ni in Sediments

Table L-1. Concentrations (μg/g) and Fractions (%) of Ni in Sediments (Spring)

point	Ni (μg/g)						% of Total				
	I	II	III	IV	V	Total	I	II	III	IV	V
1	0.33	3.01	3.58	5.02	4.79	16.74	2.0	18.0	21.4	30.0	28.6
2	0.22	5.29	4.05	6.26	5.95	21.78	1.0	24.3	18.6	28.7	27.3
3	0.19	8.32	8.41	13.83	10.91	41.66	0.5	20.0	20.2	33.2	26.2
4	0.07	1.51	1.15	0.90	1.97	5.60	1.2	26.9	20.6	16.0	35.2
5	0.19	2.04	2.09	5.58	4.14	14.04	1.3	14.5	14.9	39.7	29.5
6	0.24	2.99	2.46	5.11	5.81	16.61	1.5	18.0	14.8	30.7	35.0
7	0.05	1.76	1.92	6.20	6.30	16.24	0.3	10.8	11.8	38.2	38.8
8	0.05	0.41	0.37	0.34	1.57	2.73	2.0	14.9	13.4	12.3	57.4
9	0.05	0.17	0.28	0.42	1.24	2.16	2.1	8.1	13.0	19.5	57.3
10	0.03	0.45	0.82	2.46	3.63	7.39	0.4	6.1	11.2	33.3	49.1
11	0.00	3.75	3.83	11.37	9.47	28.41	0.0	13.2	13.5	40.0	33.3
12	0.08	1.40	1.75	5.64	6.01	14.88	0.5	9.4	11.7	37.9	40.4

Table L-2. Concentrations (μg/g) and Fractions (%) of Ni in Sediments (Summer)

point	Ni (μg/g)						% of Total				
	I	II	III	IV	V	Total	I	II	III	IV	V
1	0.17	4.35	4.47	6.82	4.73	20.55	0.8	21.2	21.8	33.2	23.0
2	0.15	4.15	3.42	5.23	5.18	18.14	0.8	22.9	18.9	28.8	28.6
3	0.06	3.17	5.68	13.98	6.39	29.27	0.2	10.8	19.4	47.8	21.8
4	0.12	2.90	1.92	3.77	3.71	12.42	0.9	23.4	15.5	30.3	29.9
5	0.09	2.34	2.35	5.91	5.23	15.92	0.6	14.7	14.8	37.1	32.8
6	0.11	2.56	2.62	7.54	6.10	18.92	0.6	13.5	13.8	39.8	32.2
7	0.00	1.96	1.94	4.14	6.33	14.38	0.0	13.6	13.5	28.8	44.0
8	0.09	0.46	0.28	0.25	1.23	2.31	4.0	20.0	11.9	11.0	53.0
9	0.04	0.69	0.81	1.97	3.35	6.86	0.6	10.1	11.7	28.7	48.8
10	0.08	1.25	1.40	4.10	5.08	11.91	0.7	10.5	11.8	34.4	42.7
11	0.20	4.97	6.02	14.59	8.52	34.31	0.6	14.5	17.5	42.5	24.8
12	0.00	2.40	2.13	5.69	6.41	16.64	0.0	14.4	12.8	34.2	38.5

Table L-3. Concentrations (μg/g) and Fractions (%) of Ni in Sediments (Autumn)

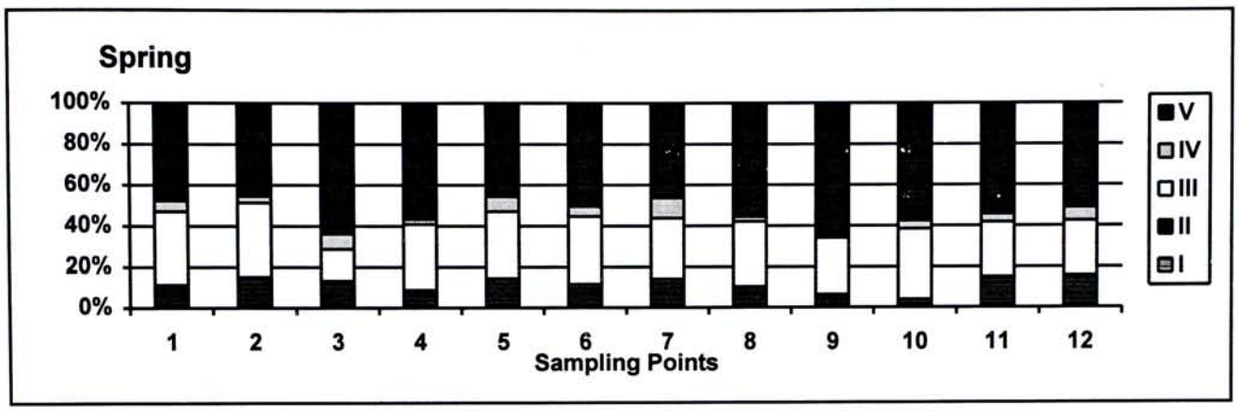
point	Ni (μg/g)						% of Total				
	I	II	III	IV	V	Total	I	II	III	IV	V
1	0.23	2.69	2.70	5.10	1.81	12.53	1.8	21.5	21.6	40.7	14.4
2	0.41	4.36	4.19	7.08	5.56	21.61	1.9	20.2	19.4	32.8	25.7
3	0.17	1.82	3.41	7.16	2.62	15.18	1.1	12.0	22.5	47.2	17.2
4	0.13	0.91	0.65	0.64	1.63	3.95	3.2	23.0	16.5	16.2	41.1
5	0.24	2.12	2.10	5.44	3.47	13.36	1.8	15.8	15.7	40.7	26.0
6	0.33	2.50	2.49	6.24	3.73	15.30	2.1	16.4	16.3	40.8	24.4
7	0.28	1.96	1.89	4.71	4.74	13.59	2.1	14.4	13.9	34.7	34.9
8	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
9	0.17	0.70	0.74	1.48	2.35	5.43	3.1	12.8	13.7	27.2	43.2
10	0.08	0.50	0.51	0.95	1.21	3.25	2.5	15.4	15.6	29.2	37.3
11	0.13	0.24	0.48	2.77	3.79	7.41	1.8	3.3	6.4	37.4	51.1
12	0.13	0.92	1.13	2.43	2.91	7.52	1.7	12.3	15.0	32.3	38.7

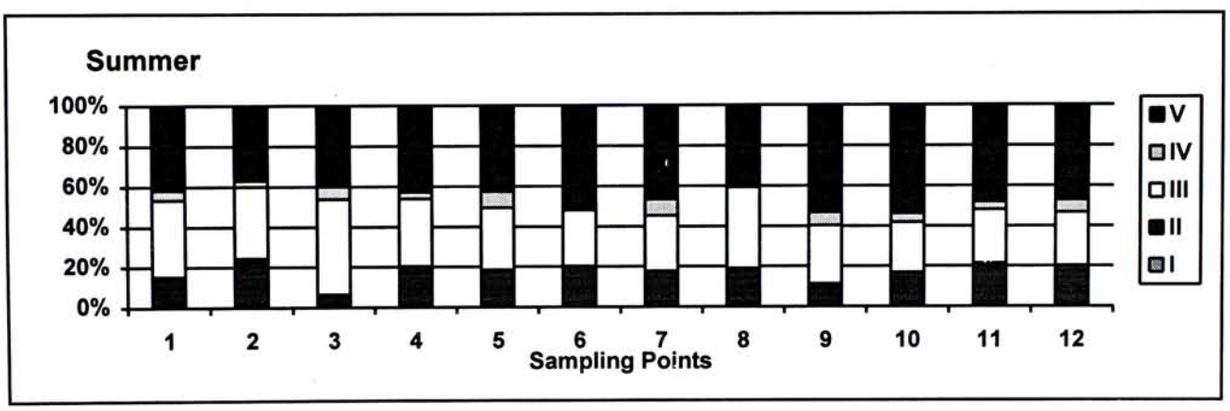
Table L-4. Concentrations (μg/g) and Fractions (%) of Ni in Sediments (Winter)

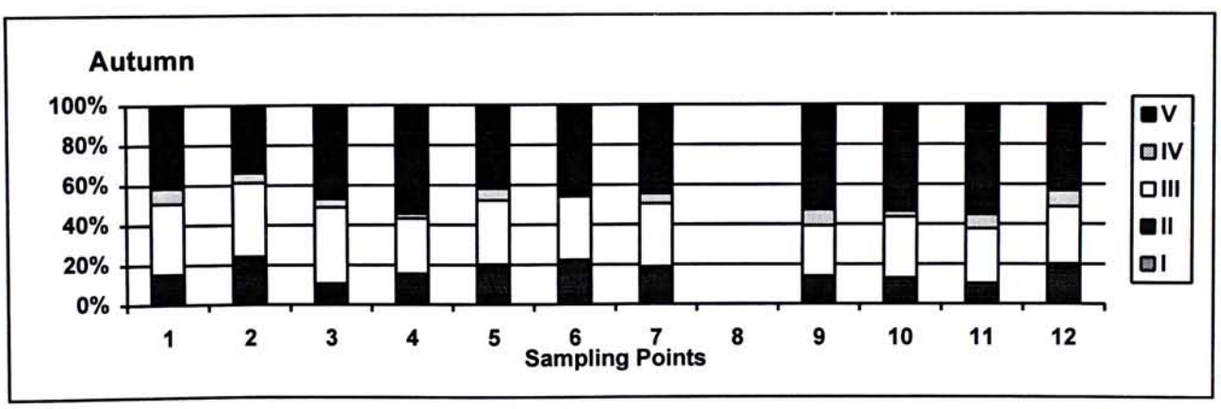
point	Ni (μg/g)						% of Total				
	I	II	III	IV	V	Total	I	II	III	IV	V
1	0.36	3.61	2.83	4.05	3.45	14.30	2.5	25.2	19.8	28.3	24.2
2	0.51	3.96	3.45	5.75	4.14	17.80	2.9	22.2	19.4	32.3	23.3
3	0.12	2.23	8.53	9.81	2.26	22.95	0.5	9.7	37.2	42.7	9.8
4	0.11	0.84	0.61	0.44	0.93	2.93	3.7	28.7	21.0	14.9	31.6
5	0.21	2.66	2.21	3.59	3.59	12.28	1.7	21.7	18.0	29.3	29.3
6	0.23	2.97	2.62	5.59	3.18	14.59	1.6	20.3	18.0	38.3	21.8
7	0.31	2.10	1.78	3.65	3.62	11.46	2.7	18.3	15.6	31.9	31.5
8	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
9	0.16	0.42	0.55	0.90	1.36	3.39	4.6	12.5	16.3	26.4	40.2
10	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
11	0.08	0.36	0.65	1.84	1.64	4.57	1.8	7.9	14.2	40.3	35.8
12	0.16	0.93	1.08	4.02	1.45	7.65	2.1	12.2	14.1	52.6	19.0

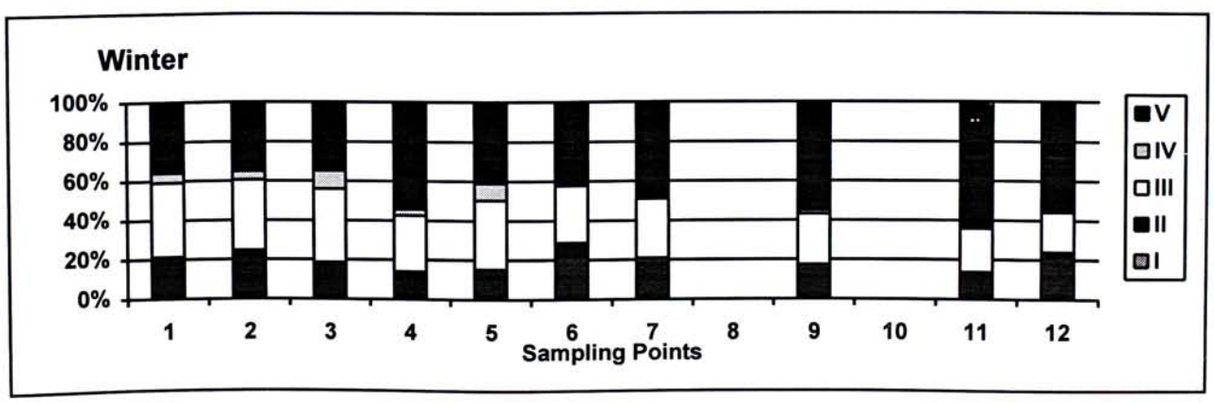
Appendix M. Fraction of Metal Speciations in the Sediments

Figure M-1. Speciation of Pb in the Sediments



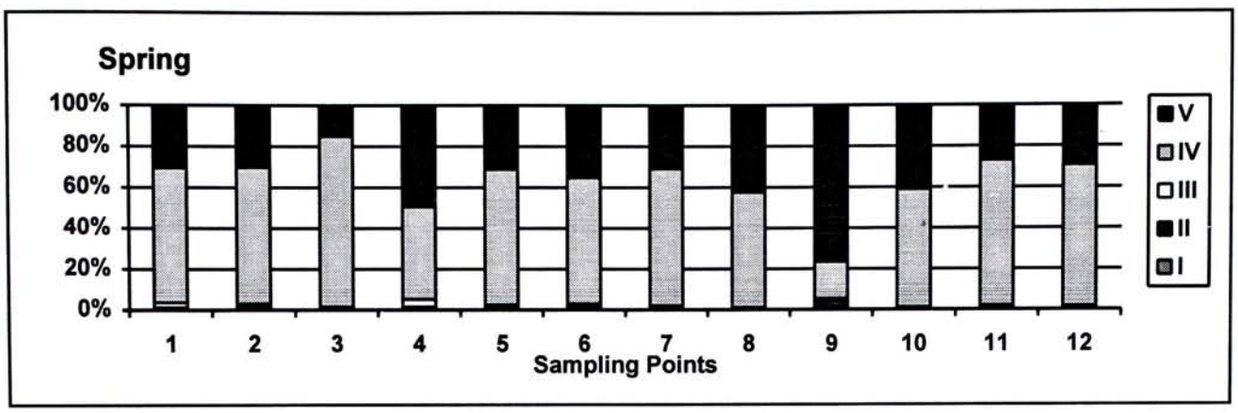


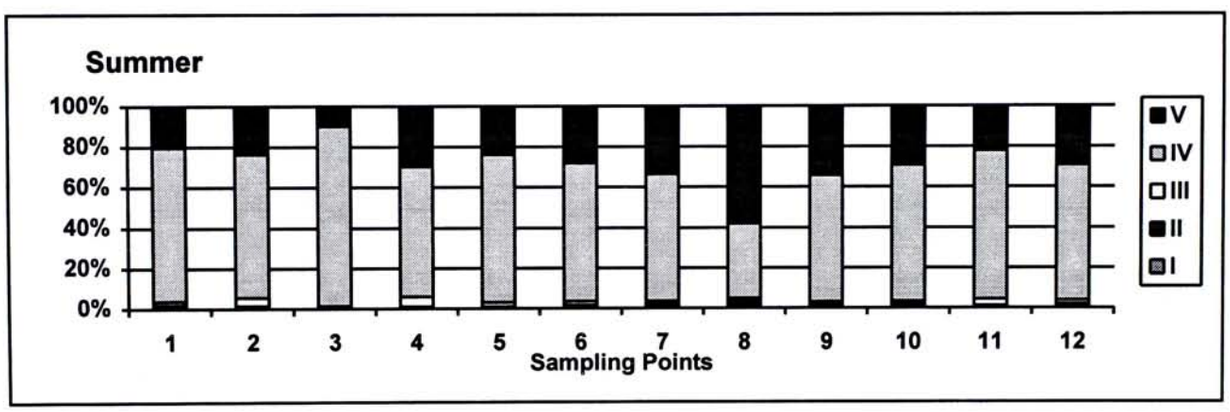


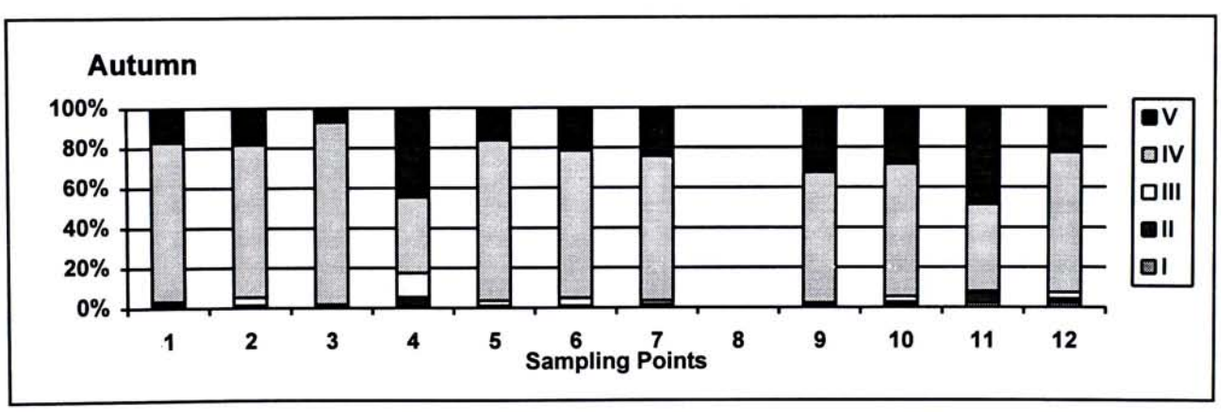


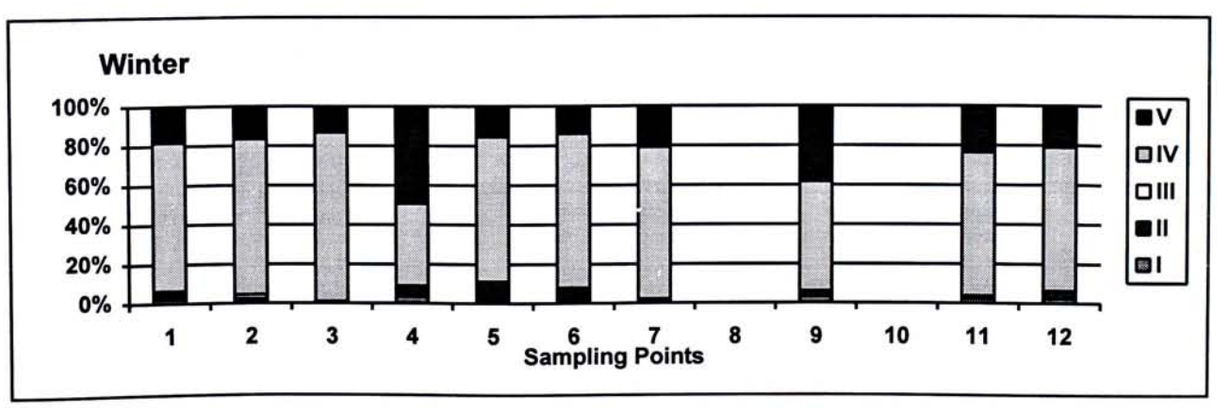
I : Exchangeable **II**: Carbonate **III** : Fe-Mn Oxides **IV** : Organic and Sulfide **V**: Residue

Figure M-2. Speciation of Cu in the Sediments



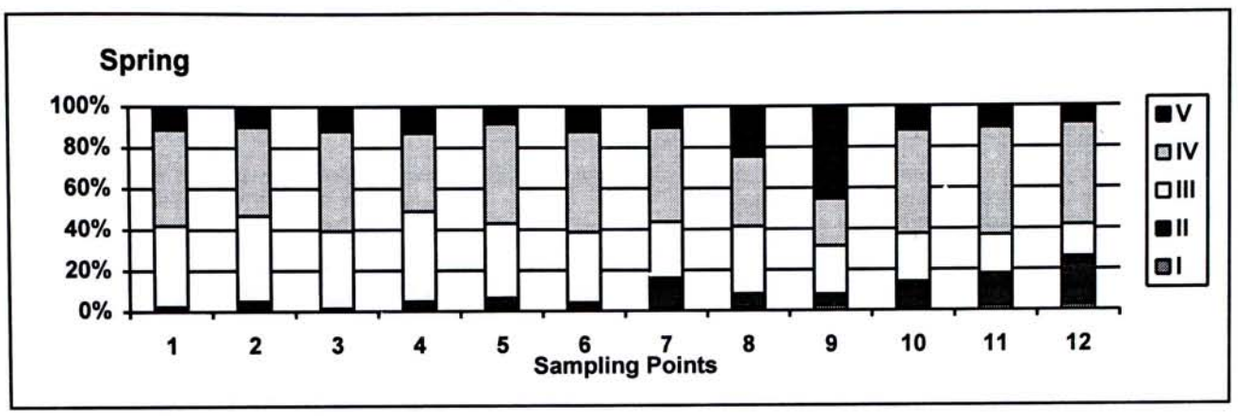


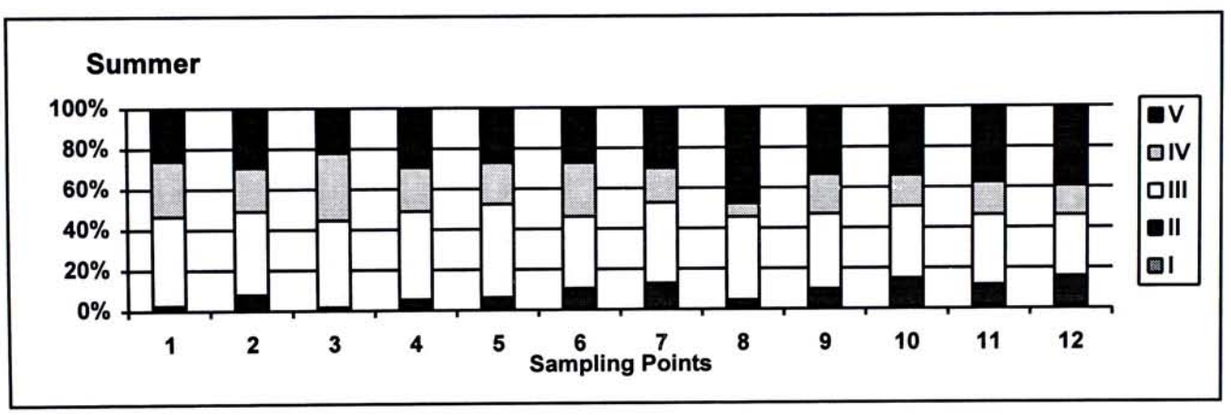


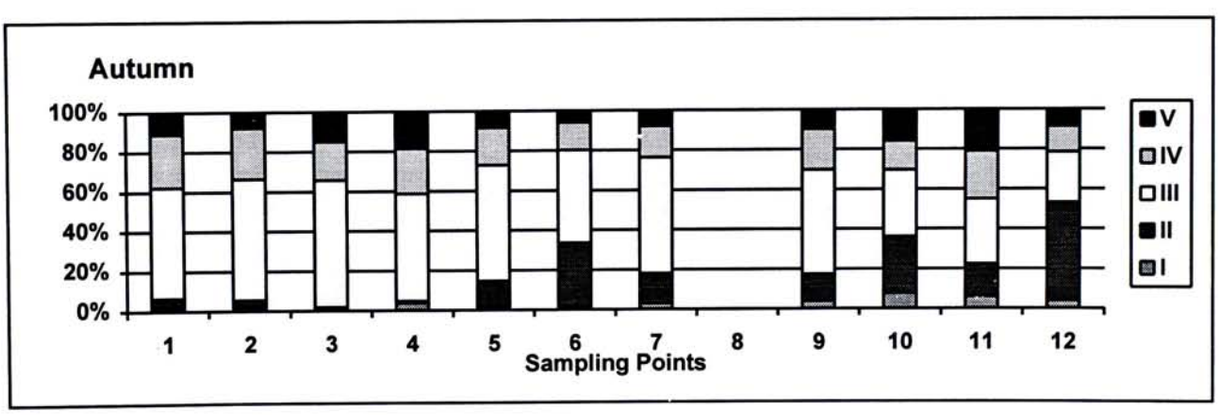


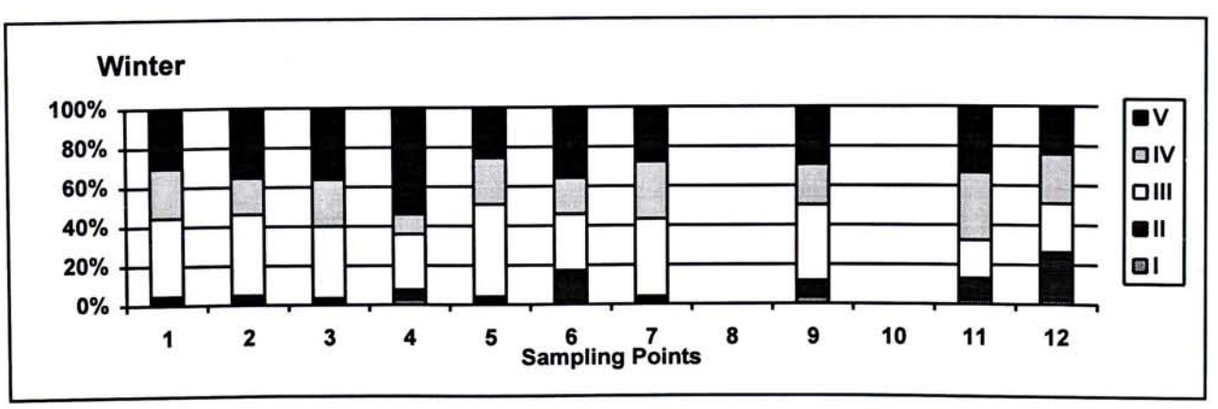
I : Exchangeable **II**: Carbonate **III** : Fe-Mn Oxides **IV** : Organic and Sulfide **V**: Residue

Figure M-3. Speciation of Cd in the Sediments



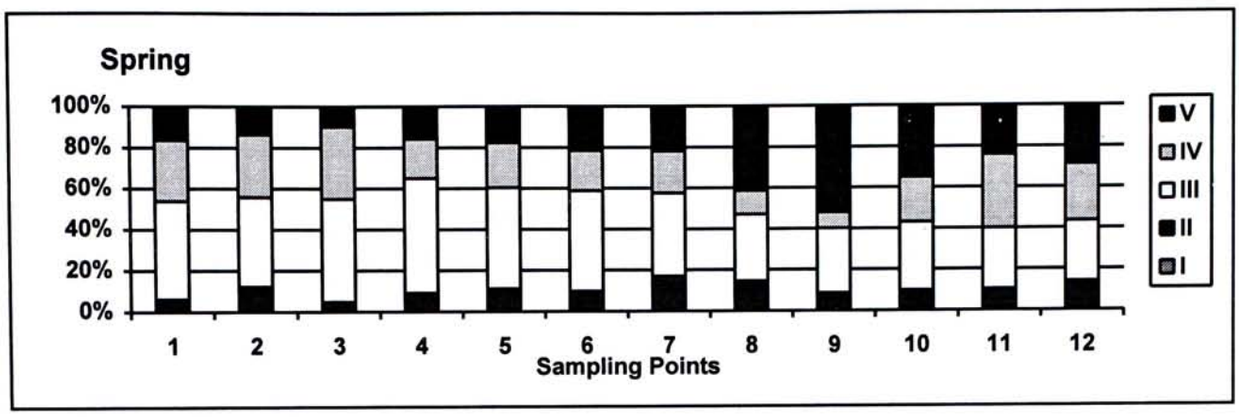


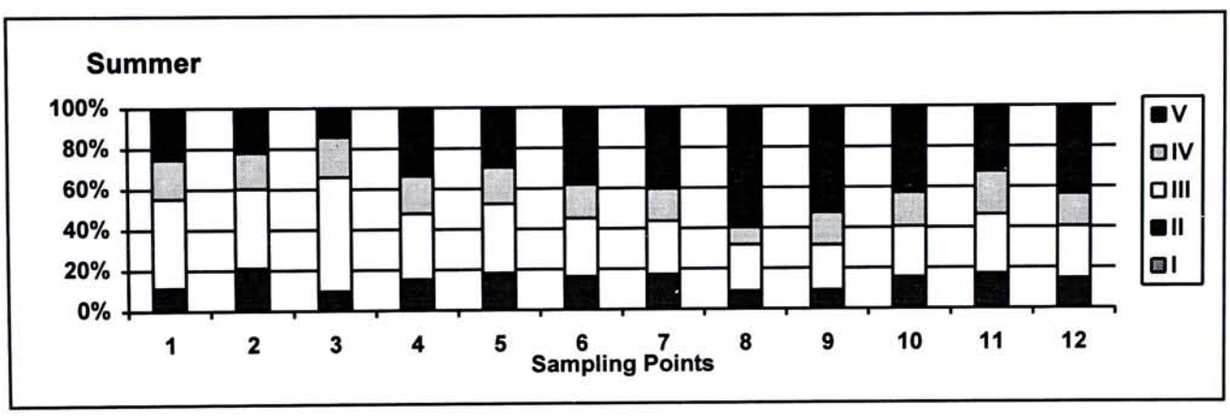


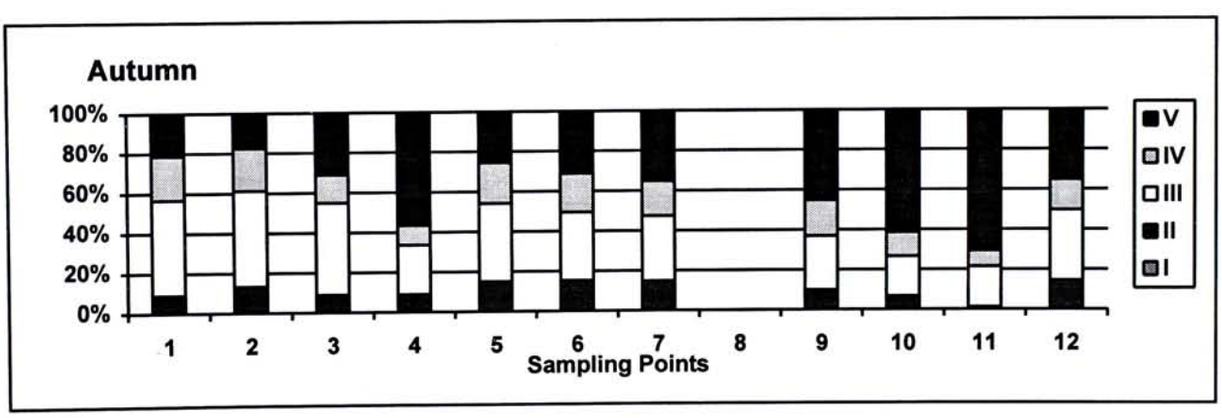


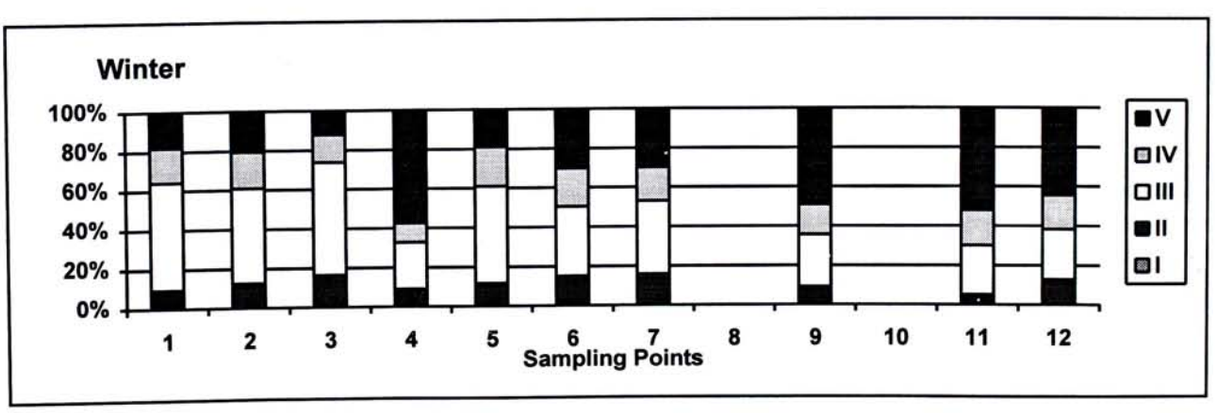
I : Exchangeable **II**: Carbonate **III** : Fe-Mn Oxides **IV** : Organic and Sulfide **V**: Residue

Figure M-4. Speciation of Zn in the Sediments



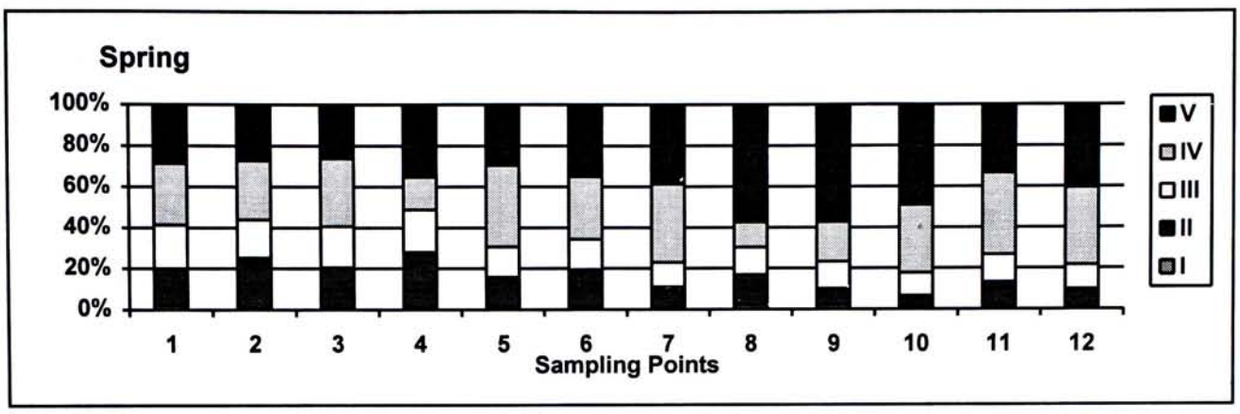


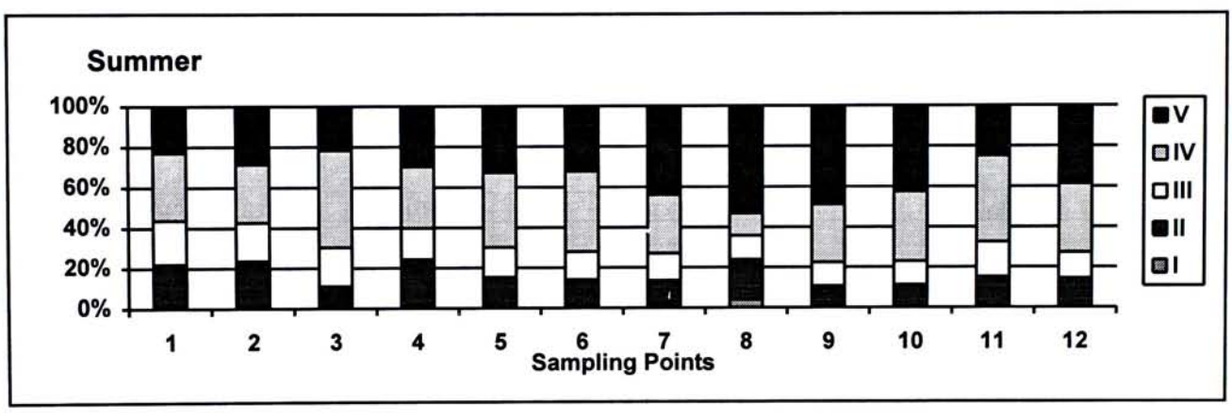


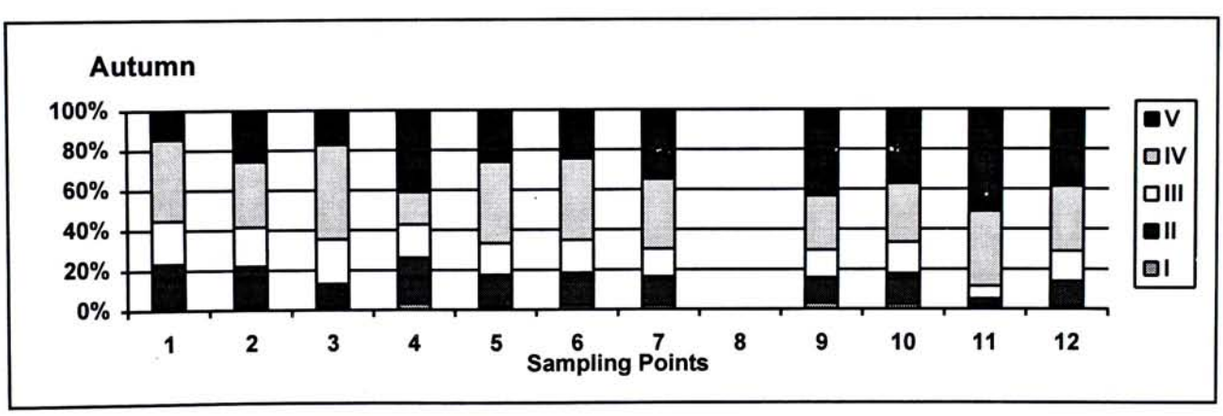


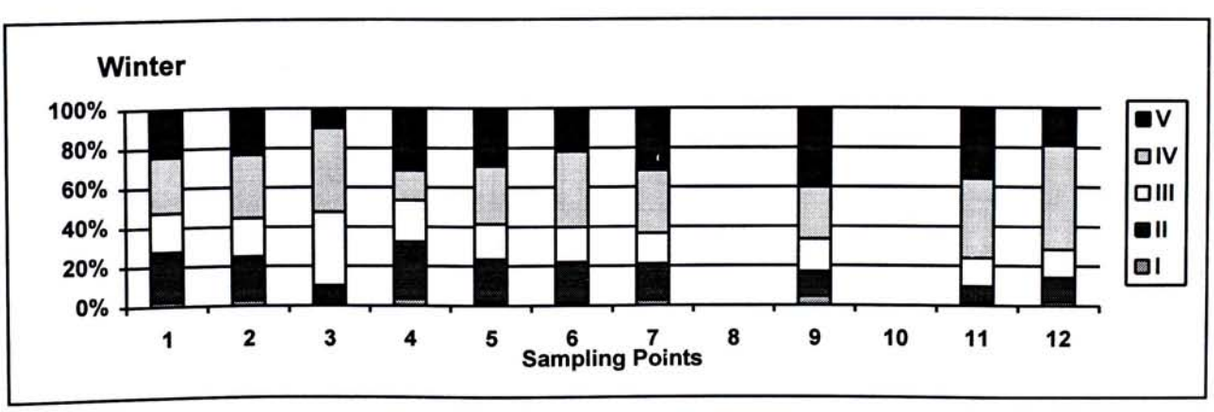
I : Exchangeable **II**: Carbonate **III** : Fe-Mn Oxides **IV** : Organic and Sulfide **V**: Residue

Figure M-5. Speciation of Ni in the Sediments









I : Exchangeable **II**: Carbonate **III** : Fe-Mn Oxides **IV** : Organic and Sulfide **V**: Residue

Appendix N. Vertical Profile of Dissolved Oxygen in the the Overlying Water

Figure N-1. DO Profile in Spring

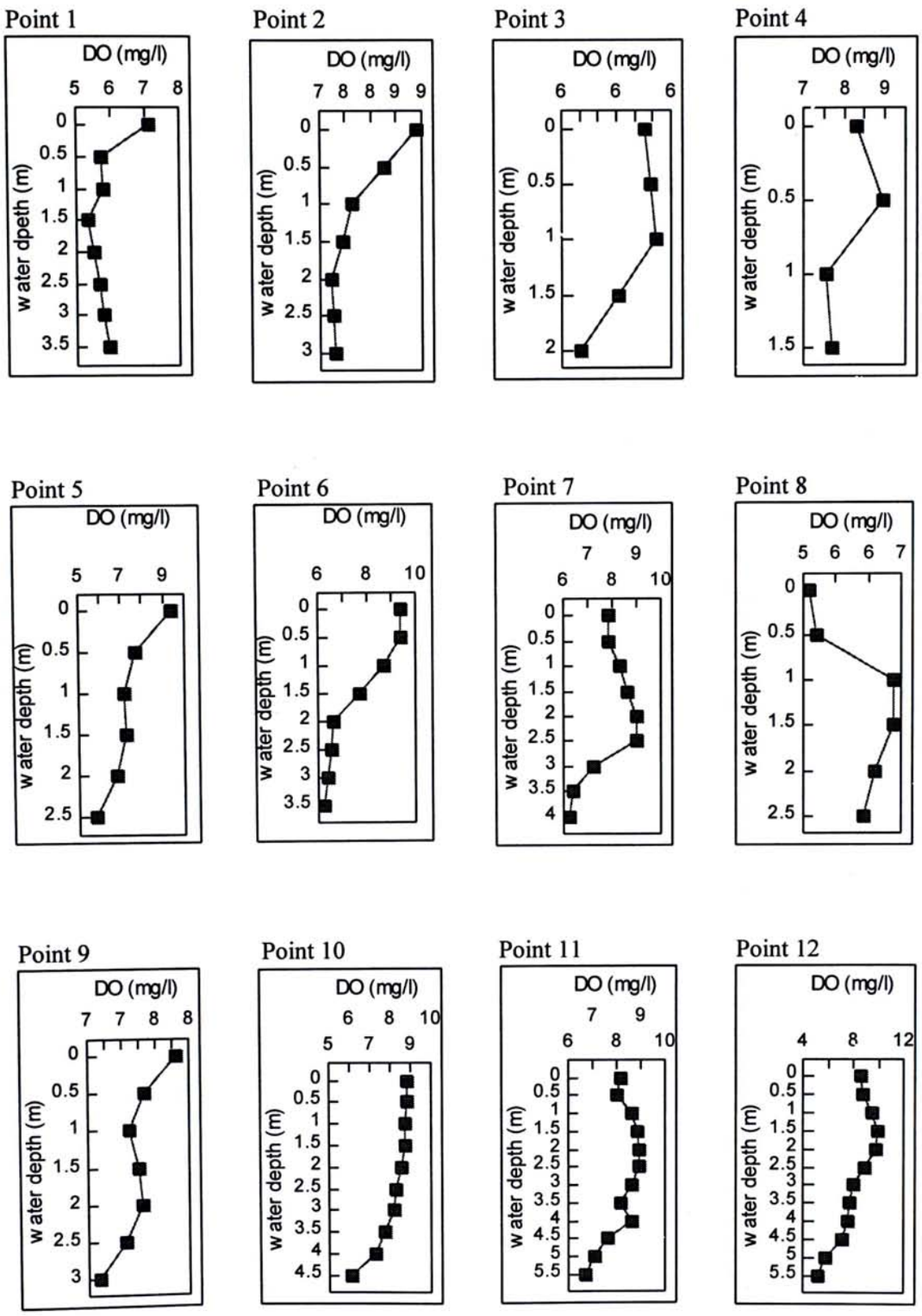
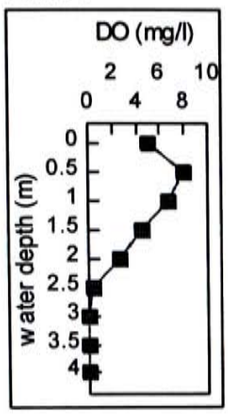
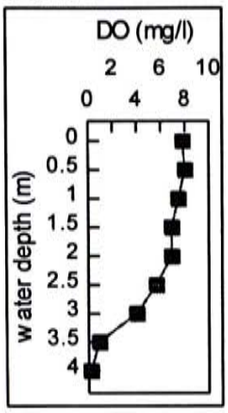


Figure N-2. DO Profile in Summer

Point 1



Point 2



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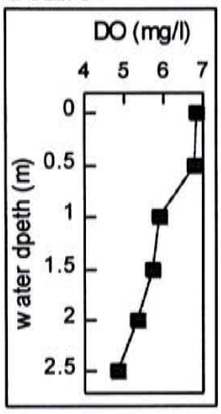

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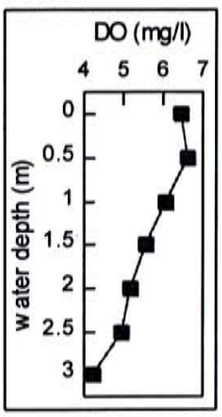

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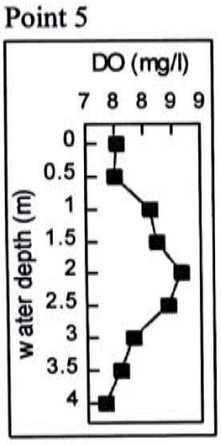

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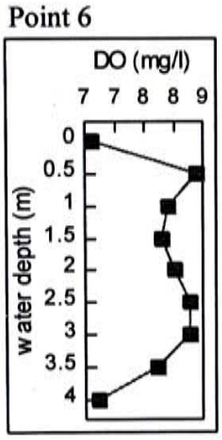

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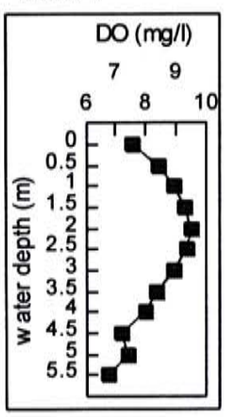

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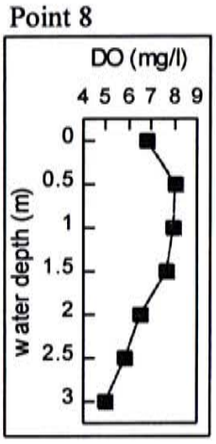

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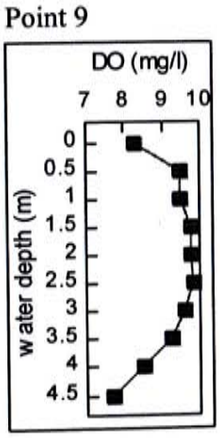

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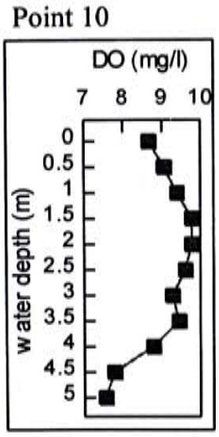

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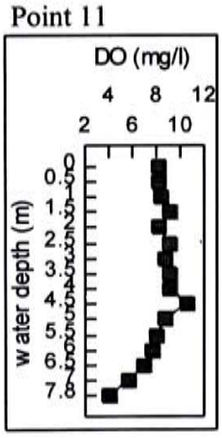

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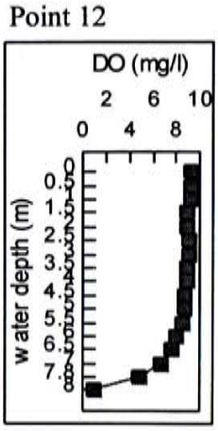

Figure N-3. DO Profile in Autumn

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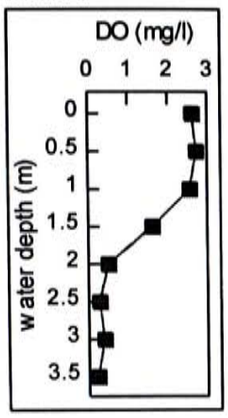

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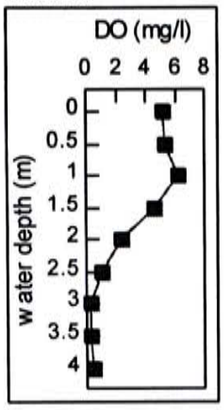

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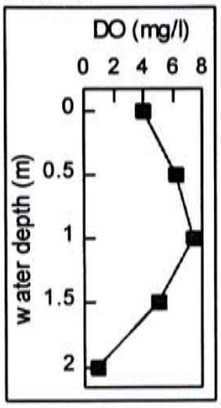

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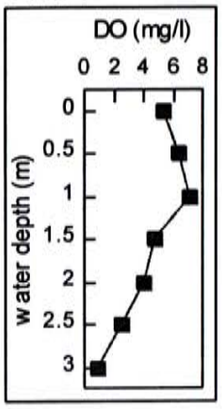

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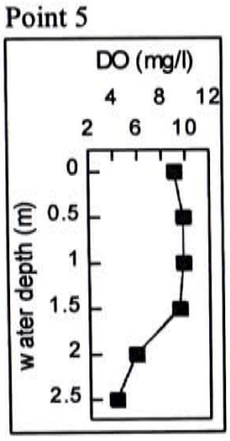

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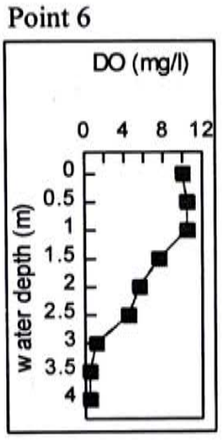

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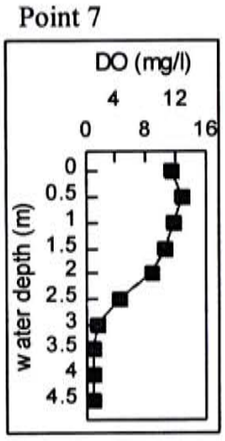

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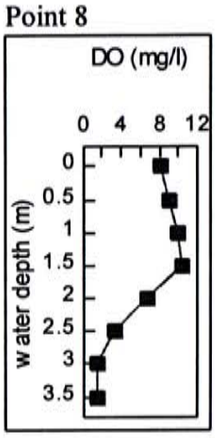

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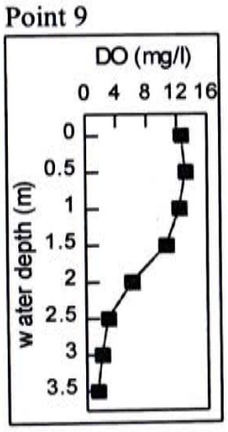

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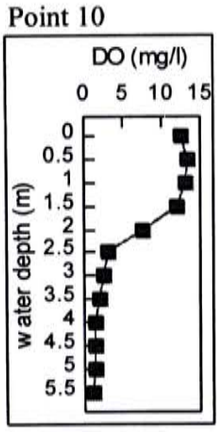

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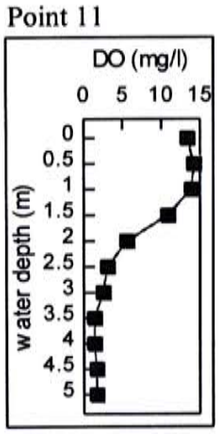

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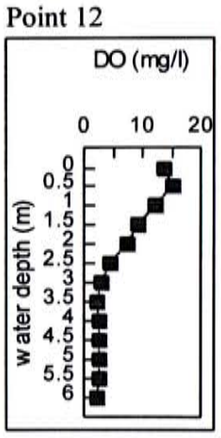

Figure N-4. DO Profile in Winter

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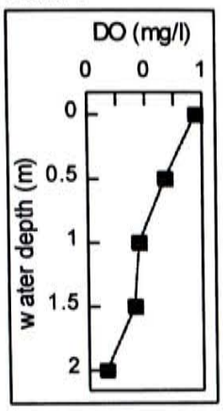

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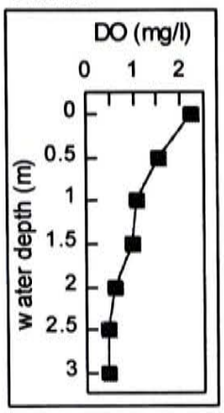

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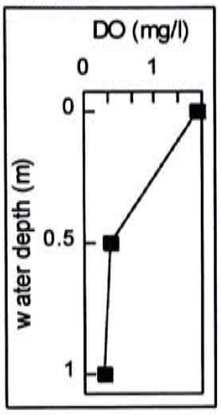

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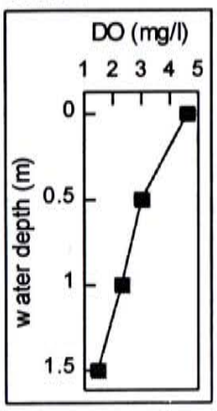

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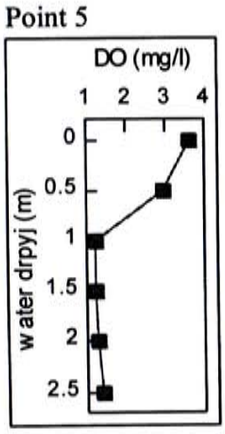

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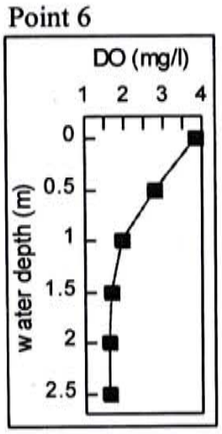

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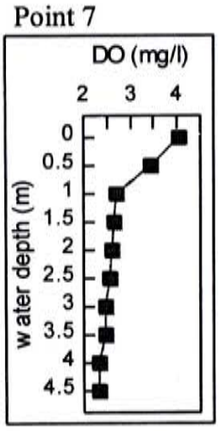

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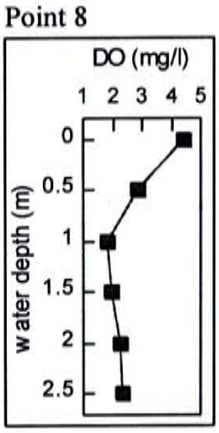

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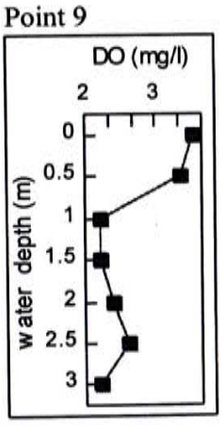

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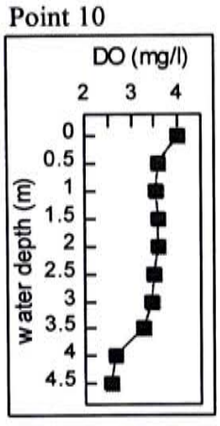

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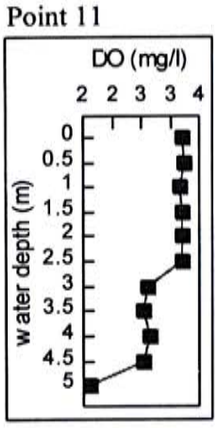

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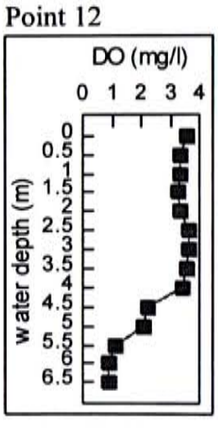


Appendix O. Vertical Profile of Salinity in the Overlying Water

Figure O-1. Salinity Profile in Summer

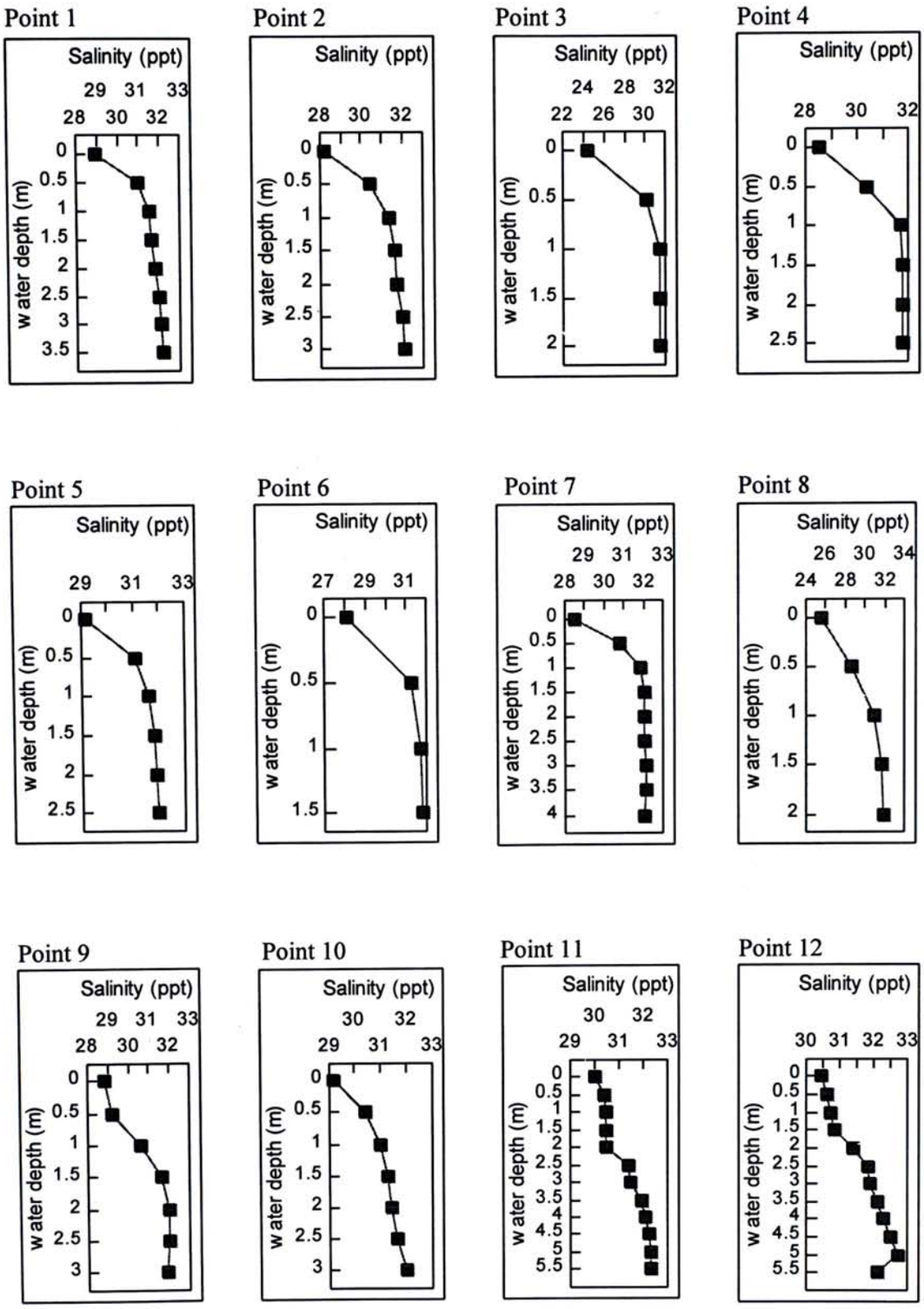
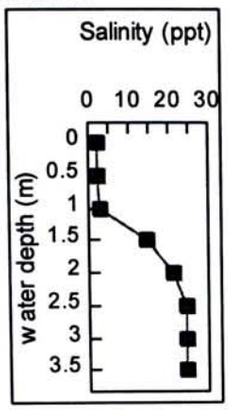


Figure O-2. Salinity Profile in Autumn

Point 1



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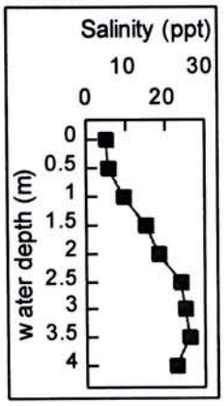

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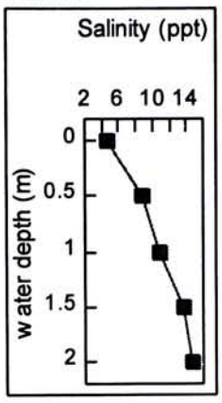

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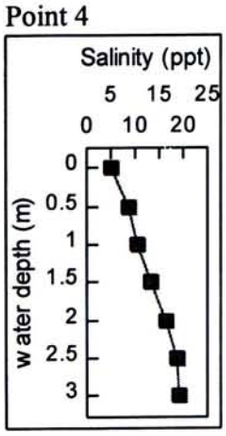

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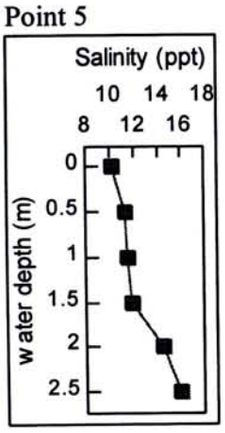

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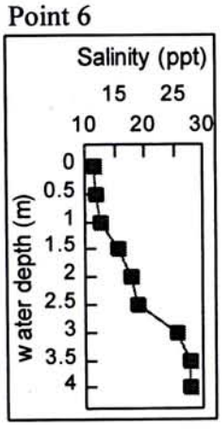

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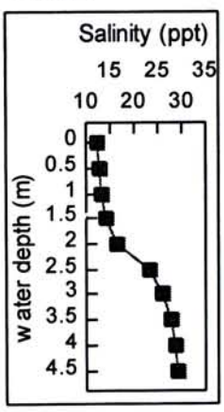

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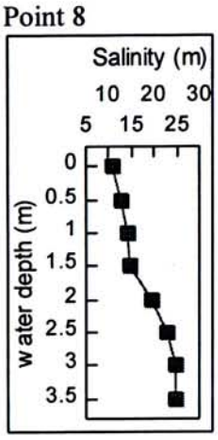

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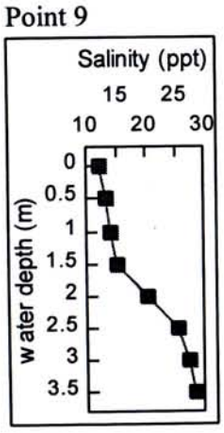

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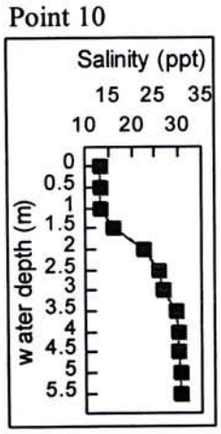

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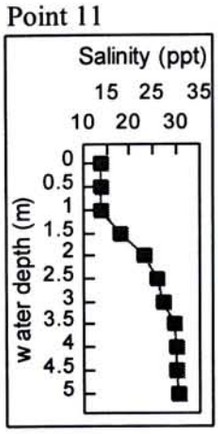

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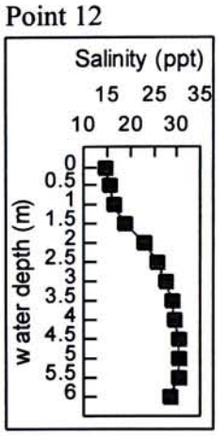
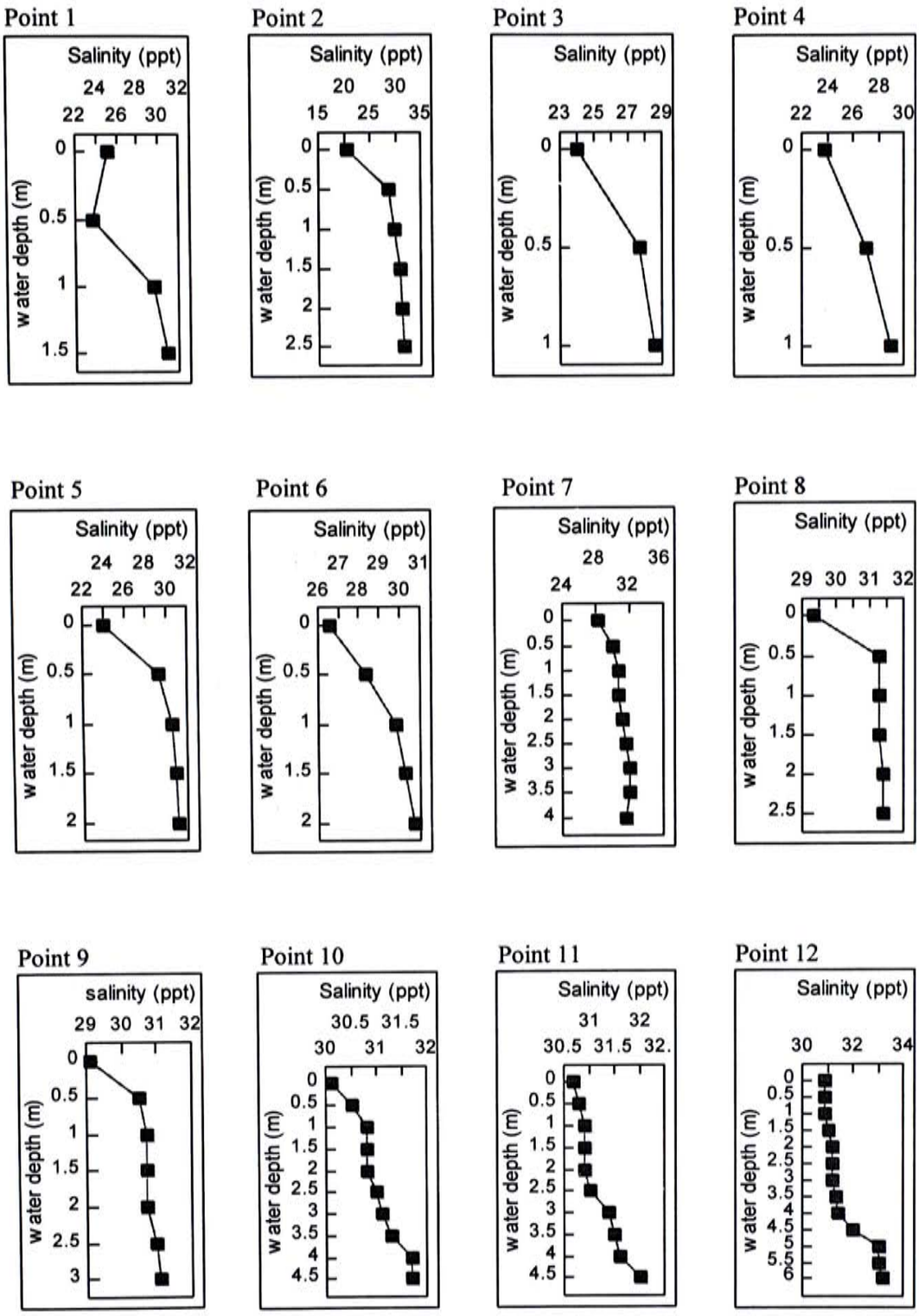


Figure O-3. Salinity Profile in Winter



Appendix P. Vertical Profile of Temperature in the Overlying Water

Figure P-1. Temperature Profile in Summer

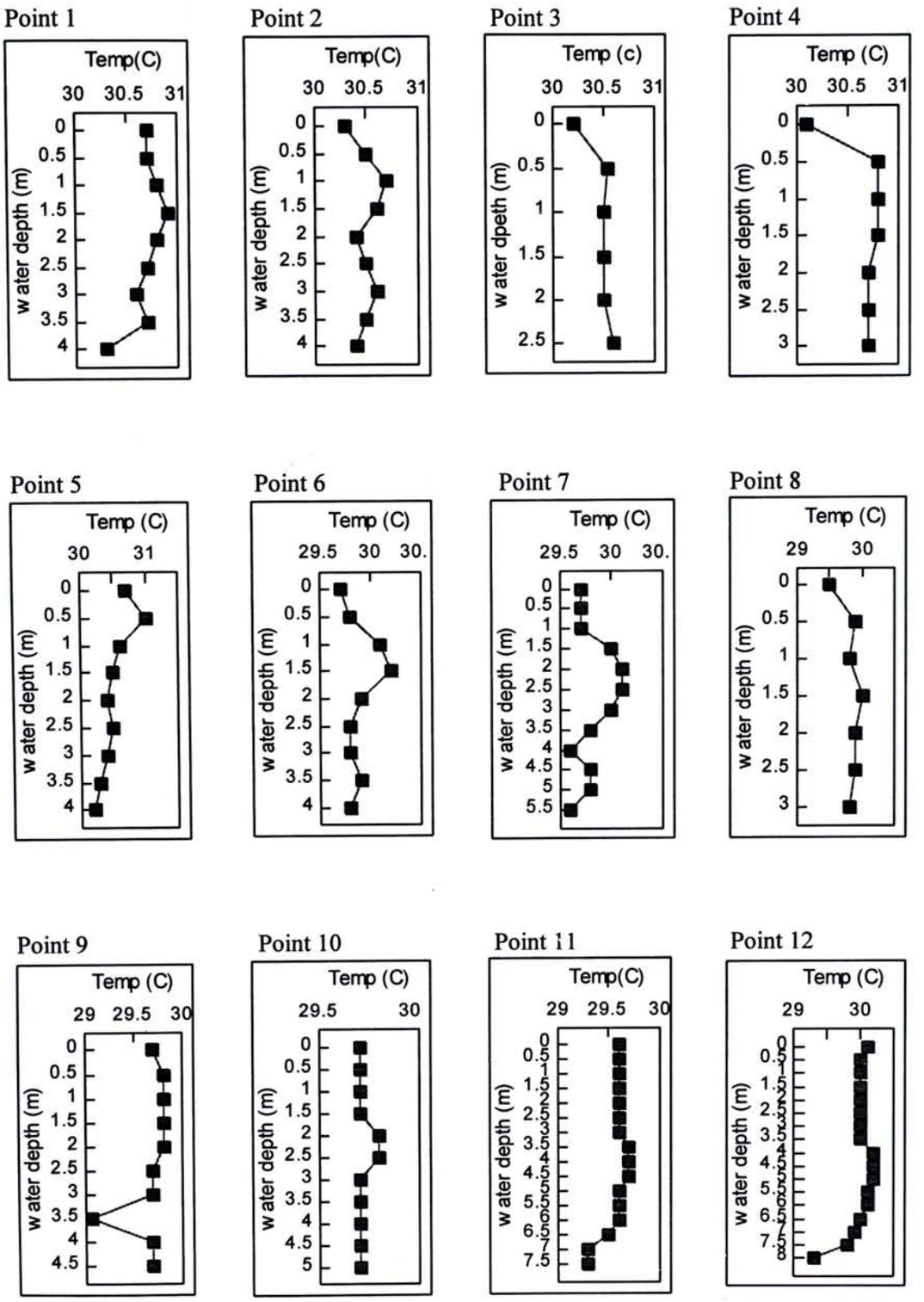


Figure P-2. Temperature Profile in Autumn

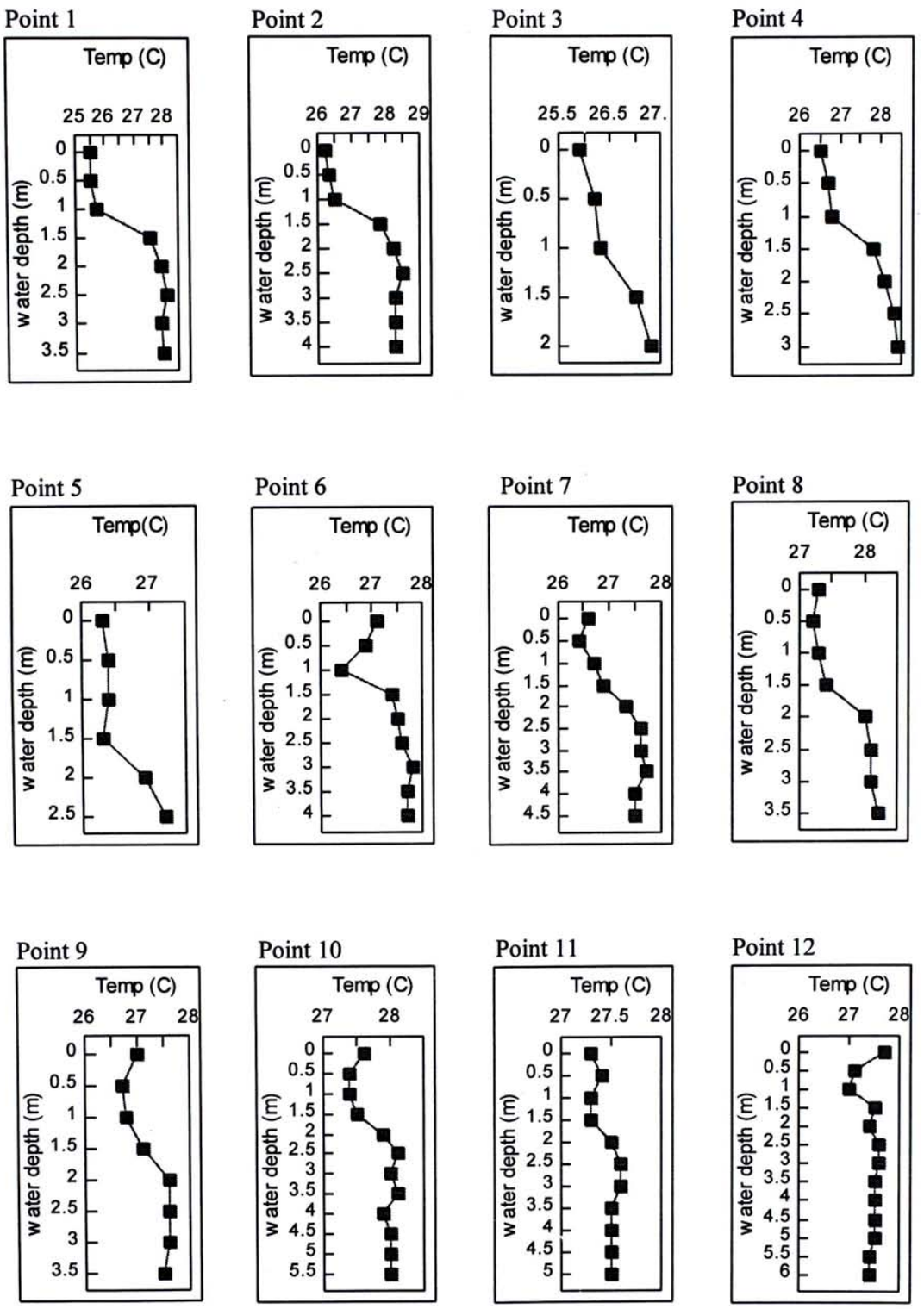


Figure P-3. Temperature Profile in Winter

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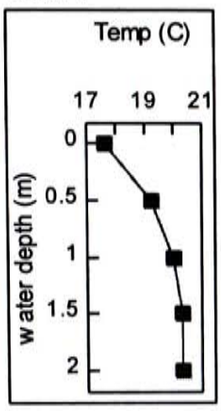

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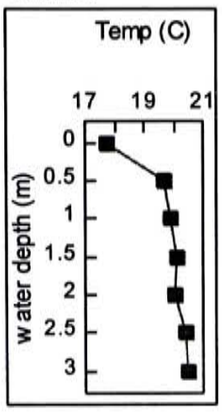

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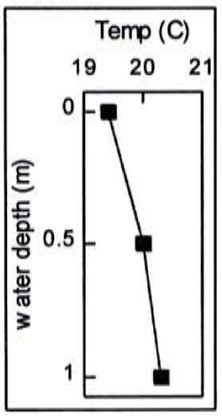

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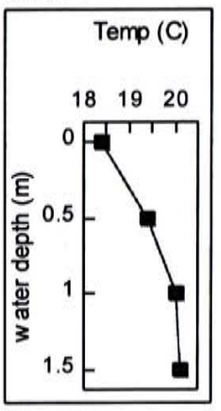

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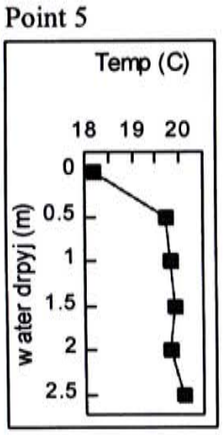

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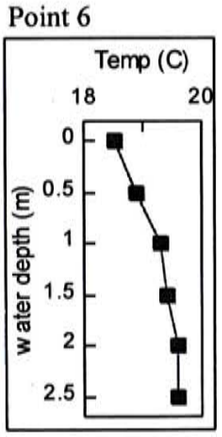
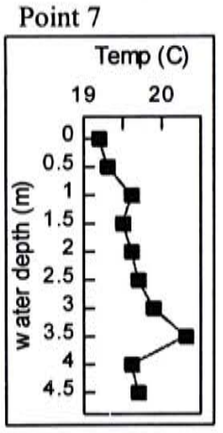


Point 7



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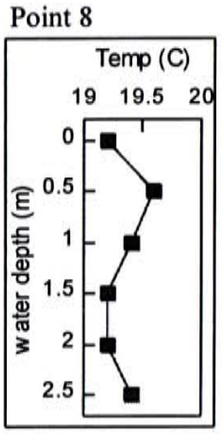

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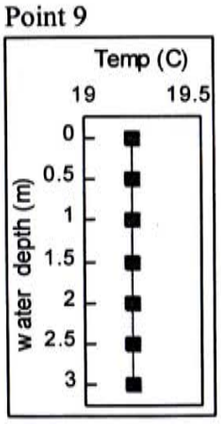

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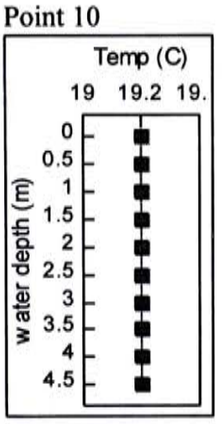

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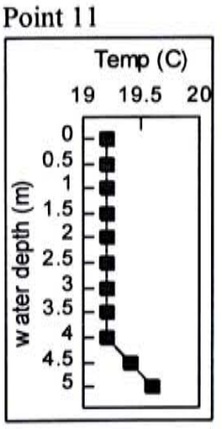

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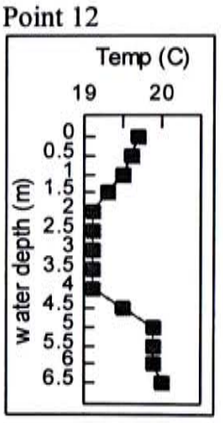


Appendix Q. Vertical Profile of pH in the Overlying Water

Figure Q-1. pH Profile in Summer

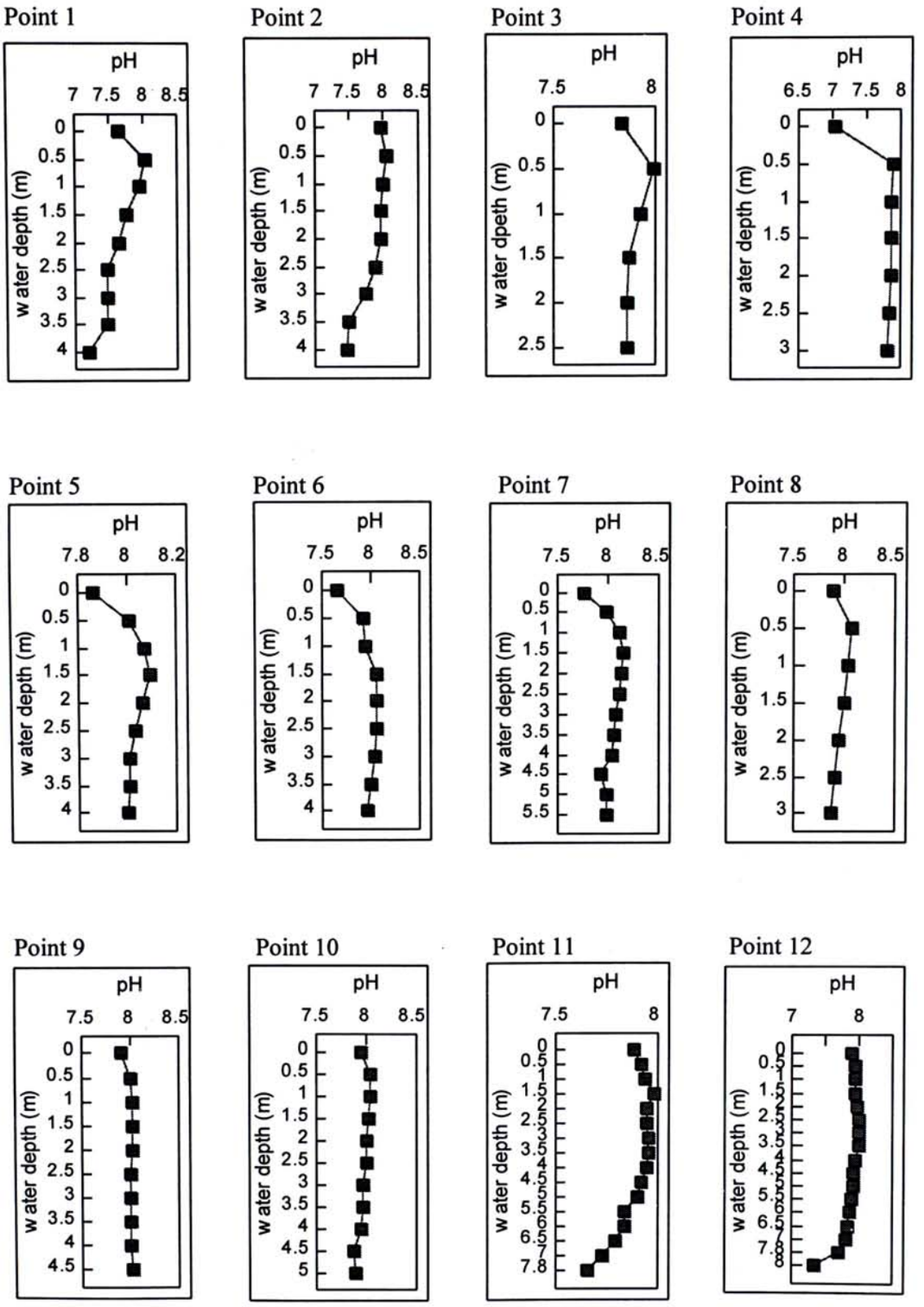
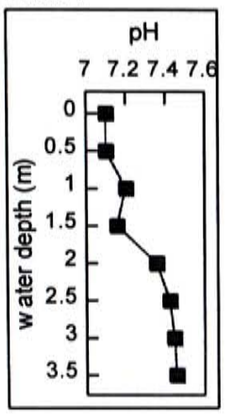


Figure Q-2. pH Profile in Autumn

Point 1



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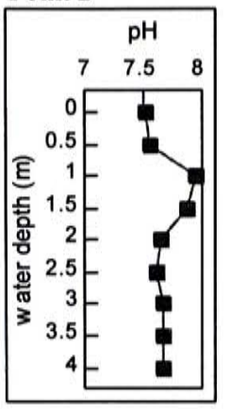
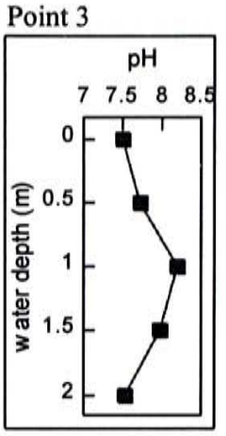
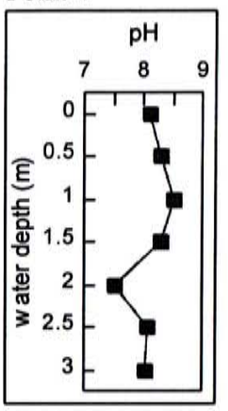


Point 3



Point 4



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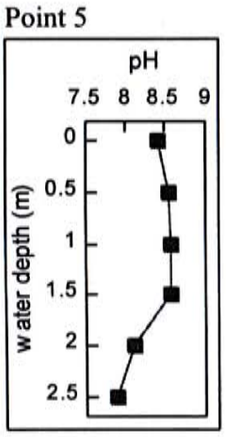
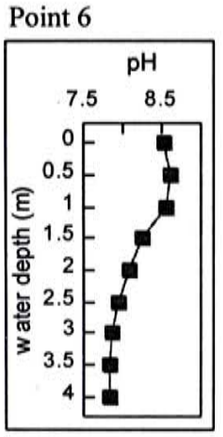


Point 6



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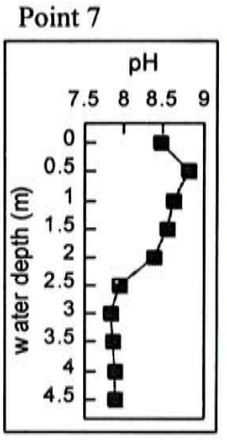
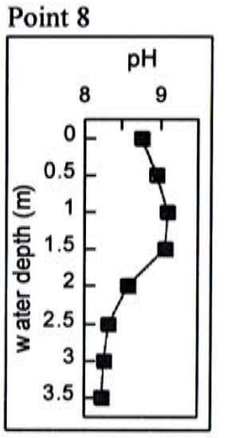


Point 8



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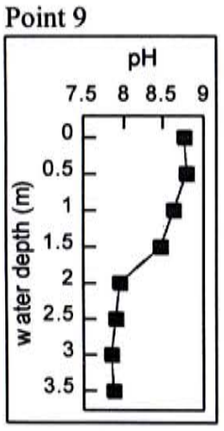

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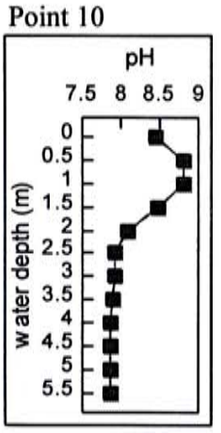

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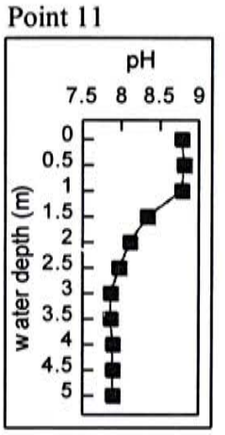

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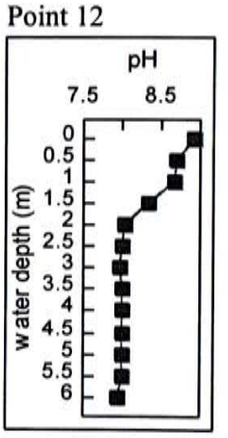

Figure Q-3. pH Profile in Winter